I.

The Osmotic Pressure of Cane-Sugar Solutions.

II.

The Semipermeable Membrane of Copper Cobalticyanide.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

ERNEST JENKINS HOFFMAN.

1906.

EASTON, PA.:
ESCHENBACH PRINTING COMPANY

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II. The Semipermeable Membrane of Copper Cobalticyanide.
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I.—THE OSMOTIC PRESSURE OF CANE-SUGAR SOLUTIONS.

INTRODUCTION.

The importance to the science of chemistry of the measurement of osmotic pressure can not be overestimated. It was from a study of the results obtained by Pfeffer,[1] and others, that van't Hoff[2] was led to put forward the hypothesis that dilute solutions obey the gas laws. Whether the analogy between solutions and gases holds for concentrated solutions could be determined only by the measurement of the osmotic pressure of such solutions. But the difficulties connected with the measurement of the osmotic pressure of concentrated solutions have seemed almost insurmountable. Attempts to repeat even the measurements of Pfeffer have generally failed.

The study of osmotic pressure was begun in this laboratory by Morse and Horn[3] in 1901. They discovered that a semi-permeable membrane could be deposited much more satisfactorily by the electrolytic method than by the diffusion method of Pfeffer. With a membrane of copper ferrocyanide they measured pressures up to 4.5 atmospheres. Failure to measure greater pressures was due principally to inability to secure the manometer in the cell.

The following year Morse and Frazer[4] made great improvements in the arrangements for securing the manometer in the cell, and also in the construction and assembling of the parts of the cell. As a result of this progress they were able to attain a pressure of about 31.5 atmospheres with a normal solution of cane-sugar.

But it soon became apparent that the real difficulty lay in obtaining a proper support for the membrane. This problem was then taken up systematically in the laboratory with the

[1] Osmotische Untersuchungen (1877).

[2] Ztschr. phys. Chem., 1, 481 (1887).

[3] Amer. Chem. Jour., 26, 80.

[4] Ibid., 28, 1.

result that a number of most satisfactory cells have been obtained.

The difficulties being thus far overcome, a careful determination of the osmotic pressure of solutions of cane-sugar was undertaken last year by Morse and Frazer. The results of their work were published[1] under the title, "The Osmotic Pressure and Freezing Points of Solutions of Cane-Sugar." From their measurements of the osmotic pressures of solutions ranging in concentration from 0.05 to 1.00 gram-molecular weight of sugar in 1000 grams of water, they found that the hypothesis of van't Hoff holds provided the standard for the solvent is the fixed mass of 1000 grams of water. Their conclusions were summed up as follows: "*Cane-sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state.*" That is to say, cane-sugar dissolved in water exerts an osmotic pressure throughout the larger volume of the solution equal to that which it would exert, as a gas, if confined to the smaller volume of the pure solvent. The experimental error in their measurements was too great to admit of deciding whether the correct standard for osmotic pressure is the volume of the solvent at the temperature of maximum density, or at the temperature at which the pressure is measured.

To test the accuracy of the inferences above drawn it is evident that very exact determination of osmotic pressure is demanded. While the results published in the above paper were as exact as experimental conditions at that time would permit, the authors were fully aware of the fact that more precise results could be obtained by eliminating or obtaining better control of certain sources of error which necessarily beset their work. In the above-mentioned paper will be found the following statement: "The measurement of the osmotic pressure of cane-sugar solutions will, therefore, be repeated at an early date, and an attempt will then be made to improve the procedure in various ways, with a view to testing more thoroughly the inferences drawn from the results of the previous work."

[1] Amer. Chem. J., 34, 1.

It was suggested by Professor Morse that, in fulfilment of this promise, a number of the measurements previously made be repeated under the more favorable conditions that now exist. Part I. of this paper contains an account and record of the results for five different concentrations. It should be mentioned here that the coöperation of two parties was absolutely necessary in carrying out these measurements of osmotic pressure, and that in this work the author has had associated with him Mr. W. L. Kennon, who has been engaged in the same line of work.

The sources of error to which particular attention was called in the above paper of Morse and Frazer were: (1) The "thermometer effects," (2) the uncertainty regarding the true capacity of the closed end of the manometer, and (3) the inversion of sugar which takes place in the cell. These difficulties will be discussed in separate parts of this paper. How and to what extent they have been overcome will there be described.

THE CELL.

As has already been stated the preparation of a porous cell suitable for the measurement of osmotic pressure has been a problem of the greatest difficulty. In great measure the problem remains yet unsettled, but so much has been accomplished in the evolution of the cell that it has been possible to produce in the laboratory a number of cells of almost perfect character.

The Construction and Assembling of the Parts of the Cell.— The details of the construction and assembling of the parts of the cell have been given in previous communications.[1] In Fig. I. the porous cell is designated by A. By means of a swiftly revolving carborundum disk, the cell while slowly turning in a chuck on the lathe is ground internally to a distance from the open end of about one-half its length. The grinding is continued until a shoulder is formed entirely around the cell of sufficient width to support the soapstone ring *b*. The letter *a* designates one of two channels which serve to give support to the cement.

[1] Amer. Chem. Jour., 28, 1; 34, 1.

The hard glass tube B which connects the cell with the manometer has the enlargements *c* and *d*, which are very necessary to prevent the tube from being pushed out through the cement of the cell or of the metal piece *o*. At *e* the tube is contracted so as to give a better hold on the rubber stopper *k*. For this glass connection the greatest care must be exercised to select a piece of tubing of the greatest strength and toughness. The frequent fracturing of this tube, usually the constricted end, has been the cause of much loss of time and labor in our work.

The soapstone ring *b* is bored and turned out on the lathe until it will fit closely over the end of the glass tube and in its place in the cell. Its lower end is beveled inward to prevent the lodgment of air.

After the ring has been put in its place on the tube, the end of the glass tube and the beveled side of the soapstone ring are covered with molten shellac. The tube and ring in an inverted position are then placed in an air-bath and heated at 110° for about five hours, and then one hour longer at 120°. Any space between the tube and the ring is thus filled with the shellac, and a tight joint obtained. The addition of shellac is continued until a covering of considerable thickness is obtained. The whole of the ground surface in the interior of the cell is then painted several times with a dilute solution of rubber in carbon bisulphide. The end of the glass tube and the soapstone ring are painted in the same way, and the ring carefully inserted in its place in the cell. The whole interior surface above the ring is again painted and the rubber vulcanized by heating in the air-bath. To insure further against leaks, shellac is then melted in the bottom of the cavity and painted with rubber solution.

The purpose of the painting with rubber is to effectually protect the cement from any contact with the solution in the cell or the water outside. The cement used is a mixture of lead oxide and glycerine containing about 10 per cent of water.

The four brass pieces, *o*, *g*, *h*, and *i* serve to hold the stopper and manometer in the cell. The piece *o* is bound to the tube B by the litharge-glycerine cement.

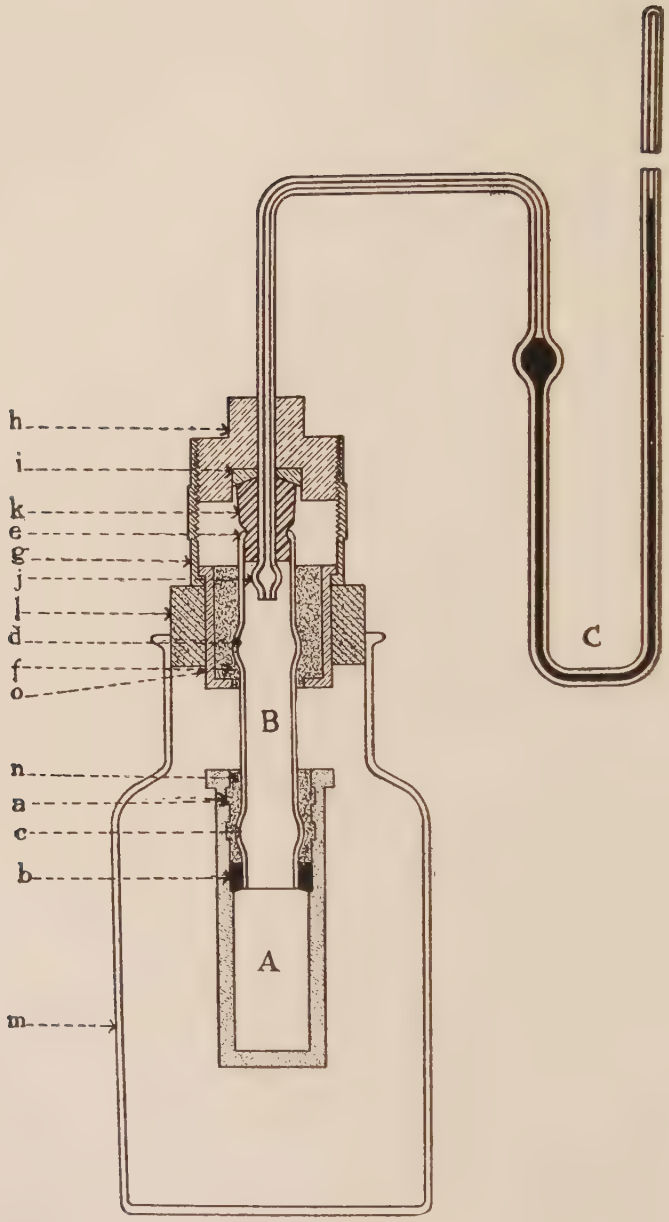

Fig. I.

The collar *g* is provided with an interior flange which locks with the exterior flange of *o*. The nut *h* is threaded to fit the interior thread of *g*. The brass piece *i* is concave at the bottom where it rests upon the stopper. This serves to prevent the stopper from moving in any other direction than toward the interior of the cell. The holes in *h* and *i* through which the manometer passes must be sufficiently large to allow considerable play for the manometer. Otherwise the manometer may be broken when the nut *h* is screwed down. The cork ring *l* holds the cell in its place in the bottle containing the water in which the cell is immersed.

The cell used in making the greater part of the measurements recorded in this paper will be designated as G. This cell before burning had a length of 9.12 cm., an external diameter below the rim of 3.58 cm., and an internal diameter at the open end of 2.51 cm. After burning its length was 8.25 cm., internal diameter at the open end 2.28 cm., external diameter just below the rim 3.20 cm., and external diameter at the bottom 2.60 cm. The cell tapered 0.044 cm. per cm. of length. Its total capacity after the assembling of all its parts was 16.1 cc.

The Preparation and Development of the Membrane.—On account of the almost ideal character of cell G the history of the preparation and development of its membrane will be given.

The air was removed from the cell walls by the usual method of endosmose. The electrodes were both of platinum. For cells of very fine texture a 0.005 normal solution of lithium sulphate is used instead of a solution of potassium sulphate of the same concentration on account of the higher rate of endosmose of the former solution. With a current pressure of 110 volts the endosmose for G was less than 40 cc. per hour. After about 500 cc. of water had passed through the walls the sulphate solution was replaced by distilled water and the electrolysis continued until all the sulphate was removed from the cell. The cell was then filled with recently boiled distilled water and placed in a vessel of the same until it was desired to deposit the membrane.

In depositing the membrane of copper ferrocyanide in the

cell the method of Morse and Horn was followed. A description of the form of apparatus in use may be had in a previous paper.[1] The anode and cathode were respectively of copper and platinum. The solution of potassium ferrocyanide placed in the cell and that of the copper sulphate outside were both of 0.1 normal concentration. The former was renewed every few minutes to prevent the accumulation of alkali and the consequent injury to the membrane formed.

A current pressure of about 110 volts has been found the most satisfactory voltage to use in the deposition of the copper ferrocyanide membrane. With a voltage of 106, cell G offered a resistance of 106,000 ohms when the electric circuit was first closed. This great resistance was due no doubt to the pores of the cell wall being filled with water. The resistance soon began to decrease, and in exactly one hour from the time of closing the circuit it had fallen to 22,660 ohms. From this point on the resistance increased until in forty-five minutes more it was 34,354 ohms. After soaking the cell over night in distilled water the membrane-forming process was continued. In one hour the resistance had reached 107,400 ohms when it began to fall slightly. The cause of this falling after a time is not known, although the phenomenon has often been observed.

At this point the cell was again soaked in distilled water until the next day when after less than two hours with a voltage of 108 the resistance had risen to 270,000 ohms and remained constant. This resistance was the highest up to that time obtained with any cell, and was regarded as the "maximum resistance" for this cell, although in several instances afterwards the resistance reached 375,000 ohms. Whenever in any subsequent reenforcement of the membrane the resistance became constant at 270,000 ohms the membrane was considered as certainly ready for a measurement of pressure. However, it has been observed that just as good a measurement can be obtained when a much lower resistance is reached. What resistance a cell and membrane will offer to the current will depend, no doubt, upon a number of conditions. But our experience has been that after a measurement of pressure

[1] Amer. Chem. Jour., 34, 1.

the soaking of the cell in water for a considerable time, at least twelve hours, is the surest way to obtain a high resistance upon again repeating the membrane-forming process. If the process is repeated early after the removal of a sugar solution from the cell it is seldom that the maximum resistance is reached. It has been our plan always after a measurement to soak the cell over night in distilled water before again attempting to reenforce the membrane for another measurement.

If the result of the first deposition of the membrane in a new cell is encouraging, the usual procedure is to set up the cell with a preliminary solution of sugar of about half-normal concentration. To this solution is added, in the case of a membrane of copper ferrocyanide, enough potassium ferrocyanide to make a tenth-normal solution, and the cell is placed in a tenth-normal solution of copper sulphate. This procedure is thought to strengthen the membrane by a process of rupture and subsequent mending in weak places. It also throws light upon the character of the cell wall.

In setting up a cell, after the insertion of the stopper, a mechanical pressure is brought to bear upon the cell and its contents by means of the nut and collar. In the case of very high concentrations the nut is repeatedly screwed down until the experimenter is satisfied that sufficient pressure has been brought to bear to prevent the removal of the stopper during the experiment. This "initial" pressure for high concentrations is often made equal to 14 or 15 atmospheres, but this pressure is never made equal to the osmotic pressure of the solution.

In the preliminary trial with cell G an initial pressure of about 2.5 atmospheres was brought to bear. The mercury continued to rise in the manometer until it indicated a pressure of about 5 atmospheres. The mercury then fell. That the membrane was ruptured considerably was shown by its low resistance at the beginning of the next membrane-forming process, and from the fact that after four hours the resistance was only 93,000 ohms. However, the cell was again set up as before, and a pressure of about 13 atmospheres was attained.

The cell was then considered ready for an exact measurement of pressure, and was set up with a 0.6 weight-normal

solution. After this measurement, in the difficult operation of removing the stopper from the cell, the exterior end of the glass tube of the cell was fractured. By exercising the greatest care we succeeded in repairing the break and in about a week the cell was again ready for use with a membrane resistance of 280,000 ohms.

Our experience has been that in the beginning of the history of a membrane there is considerable leakage and dilution during a measurement, and for this cause our first experiments were rendered unreliable and had to be repeated.

THE MANOMETER.

In Figs. I. and II. are shown the form of manometer used previous to this work. The manometer tube had a diameter of bore of about 0.5 mm., and the length of the column of enclosed air was from 400 to 450 mm. On the descending limb of the manometer was blown a bulb to serve as a reservoir for the mercury, while upon the open end was another bulb to prevent the manometer from slipping through the stopper.

This original form was subject to several serious objections. In the first place, in the very difficult operation of inserting the manometer in the cell, the enclosed air was likely to pass the bend in the tube and escape into the bulb, or the solution from the cell might get past the mercury into the air space. As a result of one or the other of these causes the manometer had to be frequently refilled, an operation requiring considerable time. This defect in the original form has been overcome by blowing another bulb in the ascending arm of the manometer directly opposite that in the descending arm. As a result of this improvement our manometers have never required refilling. The manometer is further improved by substituting for the bulb on the open end an enlargement made without increasing the bore of the tube. This renders it less difficult to replace solutions in the manometer, and, further, diminishes the chances of getting air into the bend of the tube, or makes the removal of the same a very simple matter.

But by far the most serious objection to the older manometer lies in the uncertainty regarding the capacity of the closed upper end. Since in the measurement of a pressure of

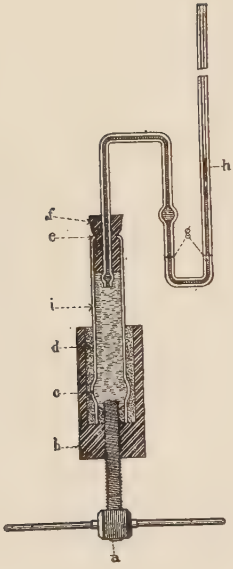

Fig. II.

about 24 atmospheres, approximately that of a weight-normal solution, the length of the air space is only about 18 mm., varying with different manometers, this uncertainty becomes a matter of most serious consequence. This difficulty has been most successfully overcome by replacing the air in the upper end with a thread of mercury. How this is done will be described in connection with the filling of the manometer. The improved form of manometer with which the measurements here recorded were made is shown in Fig. IV.

Calibration of the Manometer.—The careful calibration of the manometer is a matter of the greatest importance. The form of apparatus for carrying out this calibration is shown in Fig. II., and has been fully described.[1] The method of calibration is similar in principle to that employed for eudiometers. On the manometer are etched two lines of reference, one at *g* (Fig. II.) on the ascending arm, the other near the top of the manometer. The calibration, briefly described, is carried out as follows: After being carefully cleaned and dried the manometer is filled with pure mercury and connected with the calibrating apparatus which is also filled with mercury. A short thread of mercury (*h*, Fig. II.) is introduced, leaving a short air space between the thread and the main column of mercury. After clamping the manometer and apparatus in a perfectly vertical position, the thread of mercury is made to descend until its lower end is just opposite the line of reference *g* which will be designated as Scratch No. 1, or zero-point. The length of the thread is then determined by means of the cathetometer and standard scale. The thread is then made to ascend until its lower end occupies the place previously occupied by the upper end, and the length again determined. This procedure of placing end to end is continued throughout the whole length to be calibrated. To verify the calibration a second or third series of readings is made beginning with the same fixed point of reference. There are thus obtained all the data necessary for plotting the curve of corrections.

The manometer is then removed from the calibrating apparatus and the capillary depression determined in the usual way.

[1] Amer. Chem. Jour., 34, 1.

Filling the Manometer with Pure Air.—The next step is to fill the manometer with pure air. To do this the lower end of the manometer is connected with a reservoir of mercury which can be raised or lowered as desired. Carefully purified air is then repeatedly drawn in and expelled and finally the manometer is closed in the following way: Before drawing in the air which is to be enclosed finally, the reservoir is raised until the rubber tubing joining the manometer to the purifying apparatus is partially filled with mercury. The rubber connection is then pushed aside with the thumb and finger, breaking the mercury column. By lowering the reservoir the desired quantity of air is drawn in, and then after releasing the rubber connection a thread of mercury of the desired length is made to follow. The thread should be of such length that it shall eventually fill all space heated in the operation of sealing off the end of the manometer. After the thread has been drawn down a few inches below the top of the manometer, the manometer can be detached from the air-purifying apparatus, the mercury thread cutting off all connection between the enclosed air and that outside. By means of a small hand blowpipe a short piece of manometer tubing is then sealed on to the end of the manometer and the end of the manometer drawn out to a capillary about three or four inches in length. By raising the mercury reservoir the mercury thread is forced up until it reaches nearly to the end of the capillary. The end of the capillary is then sealed off.

The reservoir is now lowered until there is considerable diminished pressure, so that in the subsequent heating the mercury shall not be forced out of the heated portion. The end of the manometer and the mercury filling it are then heated at the point where it is desired to close the manometer. The heating with the blowpipe will necessarily volatilize some of the upper end of the thread, and the heat and vapor will force the thread down some distance from the place heated, but if the operator is very careful in his manipulation of the blowpipe, a good seal may be obtained, and upon cooling the mercury will resume its place and completely fill the space in the closed end of the manometer. The closing of the man-

ometer requires the coöperation of two persons, and is a most difficult operation, but usually after several failures it can be done quite successfully.

By thus sealing off a thread of mercury in the upper portion of the manometer all uncertainty as to volume of air is entirely removed. It is only necessary to determine the length of air column between the thread at the top and the mercury column below, making the usual correction for double meniscus. As this correction is quite considerable for the higher pressures, it is of course always taken into account.

Determining the Volume of the Enclosed Air.—After filling the manometer as above described it remains to determine the volume of the enclosed air. This is done by substituting for the reservoir of mercury a piece of tubing of the same bore as the manometer and observing the volume of the air under a number of different pressures, and reducing all observations to standard conditions. The distances between the fixed points designated as Scratch No. 1 and Scratch No. 2 are then carefully determined once for all, as is also the relation of the top of the manometer to the scratches. Data are thus obtained which render it possible if desired to use the top of the manometer also as a point of reference.

Preparation for a Measurement of Pressure.—To prepare the manometer for a measurement of pressure the open end and enlargement is painted with dilute rubber solution, and the hole in the rubber stopper to be used filled with some of the same solution. The stopper is then slipped over the enlargement to its place on the manometer. Waxed shoemaker's thread is tightly wrapped and tied around the manometer tube just above the enlarged portion as a further precaution against the slipping of the manometer upward through the stopper. This preparation should be made at least the day before the manometer is to be used in order that the rubber shall have time to dry and form a tight connection.

Before inserting the manometer in the cell, the mercury in the descending limb of the manometer, or the solution, if the manometer has been previously used for a measurement, must be replaced by the solution whose osmotic pressure is to

be determined. This is accomplished by means of a very simple form of apparatus in the shape of a U-tube filled with the fresh solution, to which suction can be applied after the tube has been attached to the manometer. This piece of apparatus serves also to remove any air that may get into the bend of the manometer.

The stopper is then inserted in the cell in the way described[1] by Morse and Frazer. Care is taken to avoid as far as possible any heating of the cell and its contents during the operation of setting it up. To give rigidity to the protruding end of the stopper and bind it closer to the manometer, waxed shoemaker's thread is tightly wound and tied around the stopper, and over this is wrapped sticky insulating tape. The nut is then screwed down on to the stopper and the cell placed in the bottle of water.

EXPERIMENTAL DATA.

The manometers used in this work will be designated as No. 4, No. 5 and No. 6. They were calibrated according to the method above described.

MANOMETER NO. 4.

Average length of mercury thread used in calibration	15.264 mm.
Weight of mercury thread	0.0409 gram
Average diameter of bore	0.50 mm.
Distance from Scratch No. 1 to top of manometer	477.25 mm.
Distance from Scratch No. 1 to Scratch No. 2	294.40 mm.
Number of calibration units of air under standard conditions, in manometer	461.34
Capillary depression	0.02 atmosphere
Correction for double meniscus	0.17 calibration unit
Total capacity from Scratch No. 1 to top	0.094 cc.

MANOMETER NO. 5.

Average length of mercury thread used in calibration	15.685 mm.
Weight of mercury thread	0.0385 gram

[1] Amer. Chem. Jour., 34, 1.

Average diameter of bore	0.48 mm.
Distance from Scratch No. 1 to top of manometer	482.58 mm.
Distance from Scratch No. 1 to Scratch No. 2	293.94 mm.
Number of calibration units of air, under standard conditions, in manometer	442.18
Capillary depression	0.02 atmosphere
Correction for double meniscus	0.16 calibration units
Total capacity from Scratch No. 1 to top	0.088 cc.

MANOMETER NO. 6.

Average length of mercury thread used in calibration	13.841 mm.
Weight of mercury thread	0.062 gram
Average diameter of bore	0.64 mm.
External diameter of manometer tube	5.1 mm.
Distance from Scratch No. 1 to top	503.91 mm.
Distance from Scratch No. 1 to Scratch No. 2	298.06 mm.
Number of calibration units of air, under standard conditions, in manometer	402.13
Correction for double meniscus	0.21 calibration unit
Capillary depression	0.02 atmosphere
Total capacity from Scratch No. 1 to top	0.166 cc.

Since manometer No. 6 has been used in the greater number of measurements recorded in this paper, the data for its calibration are given.

In Table I. column I. gives the actual readings on the scale, for the first series of observations. Column II. gives the differences between successive readings. In column III. are the actual readings on the scale, for the second series of observations, and in column IV. are the differences between successive readings of the second series. Column V. contains the average of the differences of the two series of readings, while in column VI. are found the readings on the scale that would have been obtained if the zero of the scale had coincided with that of the manometer.

Table I.—Calibration Data for Manometer No. 6.

No. of reading.	I. Readings upward on scale. (First series.)	II. Differences.	III. Readings upward on scale. (Second series.)	IV. Differences.
1	867.54	13.61	867.54	13.61
2	853.93	13.58	853.93	13.58
3	840.35	13.65	840.35	13.67
4	826.70	13.69	826.68	13.68
5	813.01	13.62	813.00	13.63
6	799.39	13.64	799.37	13.61
7	785.75	13.60	785.76	13.58
8	772.15	13.56	772.18	13.56
9	758.59	13.61	758.62	13.66
10	744.98	13.75	744.96	13.68
11	731.23	13.75	731.28	13.73
12	717.48	13.63	717.55	13.75
13	703.85	13.74	703.80	13.72
14	690.11	13.65	690.08	13.65
15	676.46	13.72	676.43	13.72
16	662.74	13.74	662.71	13.71
17	649.00	13.71	649.00	13.75
18	635.29	13.72	635.25	13.70
19	621.57	13.75	621.55	13.76
20	607.82	13.81	607.79	13.78
21	594.01	13.86	594.01	13.85
22	580.15	13.86	580.16	13.81
23	566.29	13.92	566.35	14.05
24	552.37	13.87	552.30	13.88
25	538.50	13.90	538.42	13.85
26	524.60	13.88	524.57	14.01
27	510.72	13.89	510.56	14.06
28	496.83	14.06	496.50	14.10
29	482.77	14.10	482.40	14.02
30	468.67	14.06	468.38	14.03
31	454.61	14.11	454.35	13.98
32	440.50	14.16	440.37	14.07
33	426.34	14.21	426.30	14.18
34	412.13	14.21	412.12	14.12
35	397.92	14.13	398.00	14.19
36	383.79	14.16	383.81	14.21
37	369.63	14.17	369.60	14.20
38	355.46	....	355.40	....

Table I. (*continued*).

No. of reading.	V. Average of differences of first and second series.	VI. Readings on scale calculated from zero-point.	VII. Product of number of settings by mean length of thread.	VIII. Connection values.
1	13.610	13.61	13.841	0.23
2	13.580	27.19	27.682	0.49
3	13.660	40.85	41.523	0.67
4	13.685	54.53	55.364	0.83
5	13.625	68.16	69.205	1.05
6	13.625	81.78	83.046	1.27
7	13.590	95.37	96.887	1.52
8	13.560	108.93	110.728	1.80
9	13.635	122.57	124.569	2.00
10	13.715	136.28	138.410	2.13
11	13.740	150.02	152.251	2.23
12	13.690	163.71	166.092	2.38
13	13.730	177.44	179.933	2.49
14	13.650	191.09	193.774	2.68
15	13.720	204.81	207.615	2.81
16	13.725	218.54	221.456	2.92
17	13.730	232.26	235.297	3.04
18	13.710	245.98	249.138	3.16
19	13.755	259.73	262.979	3.25
20	13.795	273.53	276.820	3.29
21	13.855	287.38	290.661	3.28
22	13.835	301.22	304.502	3.28
23	13.985	315.20	318.343	3.14
24	13.875	329.08	332.184	3.10
25	13.875	342.95	346.025	3.08
26	13.945	356.90	359.866	2.97
27	13.975	370.87	373.707	2.84
28	14.080	384.95	387.548	2.60
29	14.060	399.01	401.389	2.38
30	14.045	413.06	415.230	2.17
31	14.045	427.10	429.071	1.97
32	14.115	441.22	442.912	1.69
33	14.195	455.41	456.753	1.34
34	14.165	469.58	470.594	1.01
35	14.160	483.74	484.435	0.70
36	14.185	497.92	498.276	0.36
37	14.185	512.11	512.117	0.01
38	.....	.....	.....	....

It will be observed (column VI) that the distance covered by 37 lengths of the mercury thread was 512.11 mm. Dividing

512.11 by 37, we obtain the average length of thread = 13.841 mm. The mercury thread was therefore considered as containing 13.841 calibration units. Column VII. gives the multiple of these values corresponding to the readings contained in column VI. In column VIII. are given the differences between the corresponding values in columns VI. and VII. These differences are the correction values used in plotting the correction curve.

THE REGULATION OF TEMPERATURE CONDITIONS.

The greatest difficulty presenting itself in the exact measurement of osmotic pressure has been the maintaining of constant temperature conditions. Fluctuation in temperature during an experiment is a source of great error and must be eliminated if accurate measurements are to be obtained. This source of error has been designated as *thermometer effects* and manifests itself in the following way.

If the temperature of the room in which is placed the cell containing a solution whose pressure is being measured falls, the solution and mercury contract faster than the water can pass through the membrane to maintain the pressure which is normal to the solution, and consequently the mercury column falls to a point below that which is normal for the concentration of the solution. If the temperature of the room ceases to fall and remains stationary long enough, water will continue to enter the cell and the mercury will rise to its normal position and will remain there as long as temperature conditions are unchanged.

On the other hand, if the temperature of the room rises, the solution and mercury will expand more rapidly than the water is expelled, and we shall have too great a rise in the mercury. But if the maximum temperature remains constant sufficiently long, eventually normal conditions will be restored. It is only when the changes in the temperature of the cell contents are very slow that contraction or expansion can be compensated by the passage of the water through the membrane.

Apparatus Employed.—The means by which these tem-

perature fluctuations have been reduced to insignificant proportions are quite elaborate. For details the reader is referred to a communication[1] which is soon to appear from this laboratory.

The essential features consist in general of a large bath of more than 300 litres of water, and over this a nearly tight enclosure, in both of which uniform temperatures are maintained by constant circulation of the water and of the air, and, enclosing the whole a much larger structure, in which by means of automatically regulated electric and gas stoves uniform temperature conditions are also maintained.

The bath consists of a rectangular copper-lined wooden box, 1.24 meters long, 0.457 meter wide, and 0.66 meter deep. It is surrounded by a larger wooden box, the intervening space on all sides except the top being tightly packed with hair.

The enclosure above the bath has a height of 0.508 meter, a length about three-fourths that of the bath, and a width slightly greater than that of the bath. It has a top or cover which is hinged at the back and which can easily be raised or lowered. It contains in front a mirror-plate glass window hinged at the bottom. This house contains also double walls except on the top and on front. As in the case of the bath the spaces between are jacketed with hair. The spaces in the framework of the top are filled with hair held in place by a covering of flannel tacked to the frame. The whole top is covered with a hair mattress. The glass of the window is completely covered with a thick flannel-covered pad divided in a number of places so that by lowering any one of the curtains thus formed observations can be made without exposing more than a small section of the window. Light is thrown into the house from without. The enclosure is made as nearly air-tight as possible, by the selection of suitable lumber for its construction, by the frequent use of an elastic varnish, by sticking insulating tape over the joints, by enameling heavily the whole interior, and finally, by making the glass window to close on the inside against rubber weather strips.

The whole bath and house above together with the cathe-

[1] Amer. Chem. Jour., 36, 1.

tometer and scale used in making observations rests upon supports entirely independent of the floor or other woodwork of the laboratory.

To secure uniformity of temperature throughout the whole body of the water in the bath the water is kept in constant circulation. A lead pipe of 30 mm. internal diameter lying on the bottom of the tank extends from one end of the tank to the other, where it joins a larger vertical brass pipe which extends upwards to within a short distance from the surface of the water. By means of a small fan propeller placed in the upper end of the brass pipe, the water is constantly drawn into the lead pipe at the bottom of the tank at one end and delivered at the surface of the water at the other end. The propeller is rotated by means of friction gearing driven by a small motor. By this means so uniform a temperature is maintained in the water that differences cannot be detected on thermometers graduated to 0.°1.

To keep the air in the space above the water at a uniform temperature and as nearly as possible equal to that of the water, a similar device is used. Two lead pipes of the same size as that through which the water is pumped, one on either side of the tank, extend from the top of the enclosed space downward through the water and along the bottom of the tank to the opposite end, where they meet and connect with a larger vertical brass pipe, which in turn reaches just above the surface of the water. By means of a rotating fan the warmer air in the upper part of the house is constantly drawn through the pipes and delivered at the other end of the tank above the surface of the water. The machinery by which the pump and fan are propelled is located entirely outside the house so that the heat generated does not sensibly affect the temperature of the bath.

Fig. III. is a photograph of the bath together with a number of other pieces of apparatus used in the work. Designated by *d* is the top of the bath stripped of its upholstery; *e* is the glass window without its curtains; *f* is the cathetometer; while within the bath are seen parts of the vertical portions of the air pipes (*i* and *h*). Within the bath are also seen three

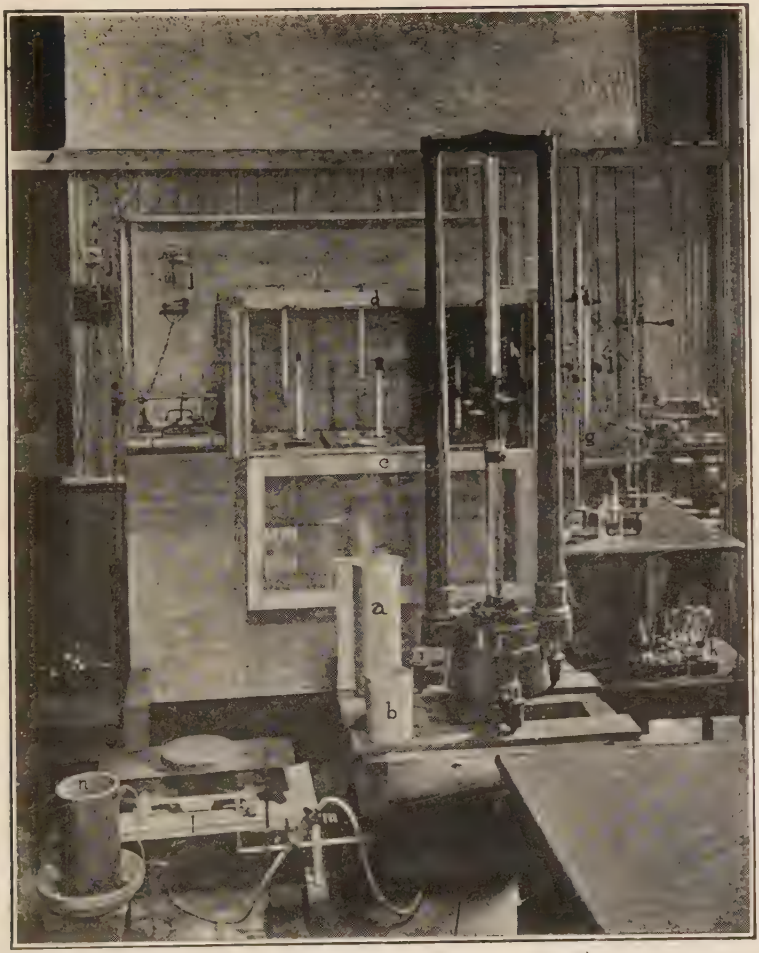

Fig. III.

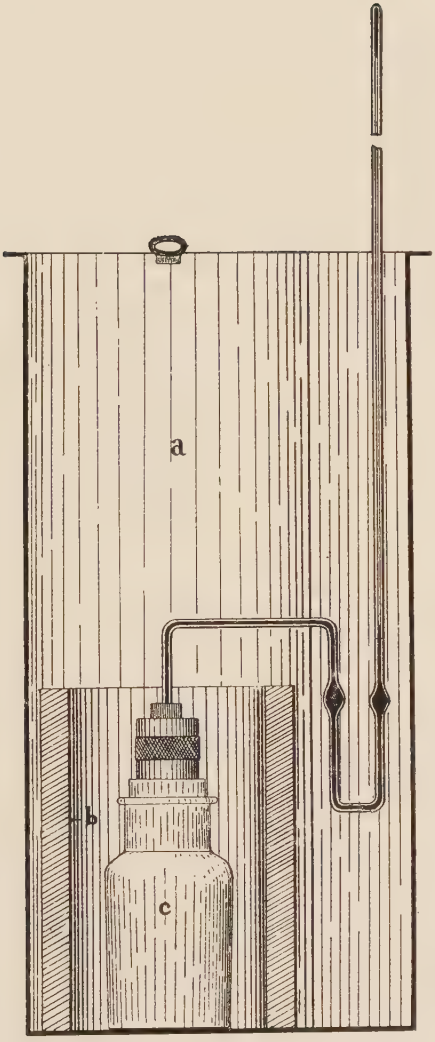

Fig. IV.

iron plates resting upon the edges of the tank and serving to hold in place the galvanized iron cans (*a*, Fig. III.), in one of which the cell is placed while a measurement is in progress. The cans are weighted down by means of heavy cast iron cylinders (*b*, Fig. III.).

In Fig. IV. are seen the can *a*, the cylinder *b*, and the bottle containing the cell, with which is connected the manometer, in their respective positions during a measurement.

During the progress of a measurement the open end of the can containing the cell is covered closely with a flannel-covered pad of hair, so that the cell located at a considerable depth below the surface of the water shall acquire the temperature of the water, while the enclosed air of the manometer takes on the temperature of the surrounding air.

The thermometers used are graduated to $0.^{\circ}2$, and were carefully compared with a thermometer tested at the Reichsanstalt.

On account of the fact that the laboratory building is heated only during working hours, the variations of temperature outside the bath were very large during the winter months, the lowest temperatures being reached at night. Hence it was found necessary to adopt means of securing more uniform temperature conditions in the room in which the bath is located, and thus avoid the effect of temperature-variation on the water and in the bath. The bath was enclosed by a framework covered on both sides with thick muslin sized with gelatin to render it less pervious to air. The enclosure was provided with doors and windows of the same construction. The space thus enclosed has a length of 3.3 meters, a width of 2 meters, and a height of 2.6 meters. To maintain a nearly constant temperature during the night, use is made of an electric stove controlled through a relay by means of an electric thermostat. To aid this stove there is provided also a gas stove regulated by means of an electric gas regulator controlled by an electric thermostat. In Fig. III. is shown the electric stove *n*; *l* is the gas stove, *m* the gas regulator, while *j*, *j*, *j*, are the thermostats.

The means above described have proved most efficient in

eliminating the source of error previously designated as "thermometer effects."

THE DETERMINATION OF INVERSION.

Having shown how two of the three great sources of error have been eliminated, it remains to consider the means that have been taken to deal with the third, the inversion of the cane-sugar in the cell during a measurement of pressure. The determinations of inversion last year by means of Fehling's solution gave results of a very dubious character, and there was reason to believe that the inversion was considerably greater than it was apparently found to be by the method employed.

It was then proposed to make use of the polariscope in determining the inversion that takes place in the cell, and it was very desirable to make the determination by simply comparing the rotation of a reserved portion of the solution whose pressure was measured with the rotation of the solution removed from the cell at the completion of the experiment.

The procedure employed to bring about this much-desired end is described at some length in what follows. It should be stated at the outset that all our solutions whose pressure have been measured are made by dissolving a gram-molecular weight of sugar, or proportional part of the same, in 1000 grams of water, all weights being corrected for air displacement. These solutions are designated as "weight-normal," etc. Further, as the basis of our calculations, the atomic weight of hydrogen is taken as unity.

The Saccharimeter.—The instrument used in this work is the Schmidt and Haensch[1] half-shade saccharimeter with triple field and double quartz-wedge compensation. The instrument is so mounted as to insure the greatest stability and rigidity, and the pinion for moving the wedges is lengthened so that the observer can move it with his hand resting on the table, a small detail that adds much to the comfort of manipulation. In this instrument a small six-volt incandescent lamp of

[1] For detailed description, see Schmidt and Haensch: Beschreibung und Gebrauchs-anweisung zu den Polarisations-Appareten (1896), and their Spezial-Preisliste (1902).

Haensch and Schmidt is employed. This lamp enclosed in the polarizer end of the saccharimeter affords a light of greater intensity than the sodium flame, with very little heating effect. To cut off objectionable rays and obtain a uniform field there is placed between the source of light and the polarizer an absorption cell of potassium bichromate solution. The end-point is determined by equality of shade.

The scale of the instrument is the Ventzke-Soleil. One hundred degrees on this scale correspond to 34.°55 (D ray), and 39°.10 (j ray), on the circular scale. Accompanying the scale is a vernier with which readings can be made to one-tenth of a degree. The "normal solution" for this instrument is one containing 26.048 grams of cane-sugar, weighed in air with brass weights, in 100 Mohr cc. at 17°.5. Such a solution polarized in a two-decimeter tube produces a rotation of exactly 100°.

Application of the Saccharimeter to the Determination of Inversion.—The application of the saccharimeter to the determination of the inversion that takes place in a solution during a measurement of osmotic pressure, by simply observing the difference between the rotation of a reserved portion of the solution and the rotation of the solution after the experiment, was made possible by the following considerations.

In the above standard solution, 26.048 grams of sugar are weighed in air with brass weights. This weight corrected for air displacement = 26.064 grams. Since 100 Mohr cc. = 100.23 *true* cc., the standard solution contains 26.004 grams of sugar in 100 *true* cc. Further, 100 *true* cc. = 100.28 cc. at 20°. Therefore, a solution of 26.077 grams of sugar in 100 cc. of solution at 20°, made up in a flask calibrated for 20°, would produce a rotation of 100° when polarized in a two-decimeter tube, or 1° rotation would correspond to 0.26077 gram in 100 cc. This solution contains 23.68 per cent of sugar. A 0.9 weight-normal solution is a 23.41 per cent solution. Since the specific rotatory power of cane-sugar does not change appreciably with even greater differences in concentration, the same value, 66.52, is taken for the "standard solution"

and the 0.9 normal solution. This value was calculated from Tollens' formula,[1]

$$[\alpha]_D^{20} = 66.386 + 0.015035p - 0.0003986p,^2$$

where p = percentage of sugar.

Hence, in a 0.9 weight-normal solution of cane sugar, each degree of rotation corresponds to 0.26077 gram in 100 cc., when polarized at 20° in a two-decimeter tube.

The specific rotatory power of invert-sugar was derived from Gubbe's formula,[2]

$$[\alpha]_D^{20} = -19.657 - 0.0361\ c,$$

where c = number of grams invert-sugar in 100 cc. C was taken equal to 0.1 and 1.0, these values being the extremes of the concentrations of invert-sugar with which we have had to deal. The value for these two extremes is — 19.67.

The ratio of the specific rotatory power of invert-sugar to that above for cane-sugar is 0.2957, or 1 gram of invert-sugar produces the same rotation, in opposite direction, that 0.2957 gram of cane-sugar produces. If 0.26077 gram of cane-sugar is inverted there will be formed 0.27450 gram of invert-sugar. Multiplying 0.27450 by 0.2957 we obtain 0.081169, the quantity of cane-sugar which is equivalent in rotating power to 0.27450 gram of invert-sugar. This quantity of cane-sugar would produce a rotation of 0°.311, or 0.27450 gram of invert-sugar causes a laevo rotation of 0°.311.

Consequently, if 0.26077 gram of cane-sugar is inverted in 100 cc. of a 0.9 weight-normal solution, there will be a loss of 1° in rotation due to the loss of 0.26077 gram of cane-sugar. The 0.27450 gram of invert-sugar formed will produce a further loss of 0°.311. The total loss, 1°.311, corresponds to the presence of 0.27450 gram of invert-sugar, or 1° loss = 0.20933 gram invert-sugar in 100 cc. of solution.

By applying the same line of reasoning to other concentrations, results are obtained, which are given in Table II.

[1] Ber. chem. Ges., 10, 1403 (1877); Landolt: Optische Drehungsvermögen.

[2] Ber. chem. Ges., 18, 2207; Z. V. Rbz.-Ind., 1884, 1345; Landolt: Optische Drehungsvermögen.

From this table it will be seen that the effect of differences in concentration such as we have in the solutions in question is very small indeed. The average of the values in column VIII. is 0.26084. For a 0.1 weight-normal solution the value is 0.26112, a difference from the average of 0.00028. This is the greatest variation from the average, corresponding to a rotation of 0°.001. This rotation is far less than can be detected on our saccharimeter. The variation from the average value of column XII. is of a still less order. Hence we feel justified in neglecting the slight effect of differences in concentration. For our purposes the averages of the values in Table II. are sufficiently accurate.

The values in Table II. hold only for the temperature of 20°. It now remains to consider the effect of changes of temperature. The procedure is essentially the same as above. The specific rotatory power of cane-sugar at different temperatures is calculated from the formula,[1]

$$[\alpha]_D^t = [\alpha]_D^{20} - 0.0144\ (t - 20).$$

Values for the specific rotatory power of invert-sugar are obtained from the formula of Gubbe,[2]

$$[\alpha]_D^t = [\alpha]_D^{20} + 0.3041\ (t - 20) + 0.00165\ (t - 20)^2.$$

Table III. contains the results for six different temperatures including 20°.

Column VIII. of Table III. contains the quantities of invert-sugar in 100 cc. which correspond to a loss of 1° in rotation. In order, therefore, to determine the quantity of invert-sugar in every 1000 grams of water in any given solution of cane-sugar, which causes a loss of 1° in rotation, the value in column VIII. must be multiplied by one-tenth the volume of the given solution.

In Table IV. will be found the specific gravities and volumes of ten weight-normal solutions. The specific gravities were interpolated from the specific gravities given by Morse and Frazer.[3]

[1] Landolt: Optische Drehungsvermögen, p. 531.

[2] Ibid., p. 526.

[3] Amer. Chem. Jour., 34, 1.

Table II.

I. Weight normality.	II. Grams cane-sugar in 1000 grams of water.	III. Percentage concentration.	IV. $[\alpha]_D^{20}$ for cane-sugar.	V. Grams invert-sugar in 100 cc. of solution.	VI. $[\alpha]_D^{20}$ for invert-sugar.
0.10	33.96	3.284	66.431	0.10–1.00	— 19.67
0.20	67.92	6.360	66.466	"	"
0.30	101.88	9.246	66.491	"	"
0.40	135.84	11.959	66.508	"	"
0.50	169.80	14.515	66.520	"	"
0.60	203.76	16.927	66.526	"	"
0.70	237.72	19.206	66.528	"	"
0.80	271.68	21.364	66.525	"	"
0.90	305.64	23.409	66.520	"	"
1.00	339.60	25.351	66.510	"	"

VII. Ratio of VI. to IV.	VIII. Grams cane-sugar in 100 cc. producing 1° rotation.	IX. Grams invert-sugar formed from VIII.	X. Laevo rotation of IX.	XI. Total loss in rotation.	XII. Grams invert-sugar in 100 cc. = 1° loss in rotation.
0.2961	0.26112	0.27487	0.3117	1.3117	0.20955
0.2959	0.26098	0.27472	0.3115	1.3115	0.20947
0.2958	0.26088	0.27461	0.3114	1.3114	0.20940
0.2958	0.26081	0.27454	0.3113	1.3113	0.20937
0.2957	0.26077	0.27450	0.3113	1.3113	0.20933
0.2957	0.26075	0.27447	0.3113	1.3113	0.20931
0.2957	0.26073	0.27445	0.3113	1.3113	0.20930
0.2957	0.26075	0.27447	0.3113	1.3113	0.20931
0.2957	0.26077	0.27450	0.3113	1.3113	0.20933
0.2957	0.26080	0.27453	0.3113	1.3113	0.20936

Table III.

Temperature.	I. $[\alpha]_D^t$ for cane-sugar.	II. $[\alpha]_D^t$ for invert-sugar.	III. Ratio of II. to I.	IV. Grams cane-sugar in 100 cc. = 1° rotation.
18°	66.53	— 20.27	0.3047	0.26072
19°	66.51	— 19.97	0.3003	0.26080
20°	66.50	— 19.66	0.2958	0.26084
21°	66.49	— 19.36	0.2912	0.26088
22°	66.47	— 19.06	0.2867	0.26096
23°	66.46	— 18.74	0.2820	0.26100

Temperature.	V. Grams invert-sugar formed from IV.	VI. Laevo rotation of V.	VII. Total loss in rotation.	VIII. Grams invert-sugar in 100 cc. = 1° loss in rotation.
18°	0.27445	0°.3207	1°.3207	0.20780
19°	0.27453	0°.3160	1°.3160	0.20861
20°	0.27457	0°.3114	1°.3114	0.20937
21°	0.27462	0°.3065	1°.3065	0.21019
22°	0.27470	0°.3018	1°.3018	0.21102
23°	0.27474	0°.2968	1°.3968	0.21186

Table IV.—Weight-Normal Solutions of Cane-Sugar.

Weight-normal concentration.	Grams of sugar in 1000 grams of water.	Specific gravity at 20°.	Volume. at 20°.
0.10	33.96	1.01283	1020.86
0.20	67.92	1.02515	1041.72
0.30	101.88	1.03687	1062.70
0.40	135.84	1.04814	1083.67
0.50	169.80	1.05900	1104.62
0.60	203.76	1.06942	1125.62
0.70	237.72	1.07947	1146.60
0.80	271.68	1.08906	1167.68
0.90	305.64	1.09833	1188.75
1.00	339.60	1.10728	1209.81

Table V. gives the quantity of invert-sugar in 1000 grams of water, which causes the loss of 1° in rotation at different temperatures. The transition here made from a volume to a weight basis is necessary because the solutions whose osmotic pressure are measured are made by dissolving the given weight of sugar in 1000 grams of water.

It will be observed that in the values given in Table V. no account is taken of the changes in volume that occur at any other temperature than 20°. By calculation we have found that for the given temperatures such omission does not affect the second decimal place. For this reason, and for the further reason that we do not have at hand satisfactory data for making these slight corrections, we have used the volume at 20° as the volume at all temperatures between 18° and 23°, and tabulated the results to only two decimal places.

Table V.—Invert-Sugar in Grams per 1,000 Grams of Water, which Produces a Loss of 1° in Rotation.

Weight-normal concentration.	Temperature.					
	18°.	19°.	20°.	21°.	22°.	23°.
0.10	2.12	2.13	2.14	2.15	2.15	2.16
0.20	2.16	2.17	2.18	2.19	2.20	2.21
0.30	2.21	2.22	2.23	2.23	2.24	2.25
0.40	2.25	2.26	2.27	2.28	2.29	2.30
0.50	2.31	2.32	2.32	2.33	2.34	2.35
0.60	2.34	2.35	2.36	2.37	2.38	2.38
0.70	2.38	2.39	2.40	2.41	2.42	2.43
0.80	2.43	2.44	2.44	2.45	2.46	2.47
0.90	2.47	2.48	2.49	2.50	2.51	2.52
1.00	2.51	2.52	2.53	2.54	2.55	2.56

By the use of Table V. the correction for inversion in a pressure cell can be easily made. The rotation of the original solution and that of the solution removed from the cell after an experiment are determined in a two-decimeter tube. The loss in rotation in degrees multiplied by the value given in the table for the given concentration at the temperature of polarization gives the concentration of invert-sugar in grams per 1000 grams of water. The osmotic pressure that would be produced by one-half this quantity of invert-sugar is the correction that must be deducted from the observed osmotic pressure.

The accuracy of the above deductions was tested by a number of experiments. The method employed can best be shown by taking a particular experiment. All weights given are weights in a vacuum, and, unless otherwise stated, it is to be understood that polarizations were made in two-decimeter tubes.

A 0.10 weight-normal solution of cane-sugar containing 33.96 grams of sugar in 1000 grams of water gave a rotation, at 19°, of 12°.73. The volume of this solution at 20° was 1020.86 cc. A second solution was then made containing 3.396 grams of sugar less per 1000 grams of water than the first solution. The rotation at 19° was 11°.48. By interpolation from volumes of Table IV. the volume of this solution was found to be 1018.76 cc. at 20°. The rotation of the latter solution was, therefore, greater than it would have been had there been no change in volume due to the difference of 3.396 grams of sugar. From the proportion,

$$1018.76 : 1020.86 :: X : 11.48,$$

$X = 11.46$, the rotation of 30.564 grams of cane-sugar in 1020.86 cc. of solution.

$12.73 - 11.46 = 1.27$, which is the loss in rotation in a 0.10 weight-normal solution due to loss of 3.396 grams of sugar.

3.396 grams of sugar were then inverted by Clerget's method, the solution made up to 1000 cc., and polarized at 20° in a four-decimeter tube. The laevo rotation was 0°.8. This value divided by 2 gives the rotation of 3.5748 grams of invert-

sugar in 1000 cc. of solution, at 20°, in a two-decimeter tube. From the proportion,

1020.86 : 1000 : : 0.4 : X,

X = 0.39, the rotation of 3.5748 grams of invert-sugar in 1020.86 cc. of solution. Dividing 3.5748 by the sum of 1.27 and 0.39, we obtain 2.15, the weight of invert-sugar that must be present in a 0.10 weight-normal solution of cane-sugar to cause a loss of 1° in rotation. This value agrees very closely with the value given in Table V.

In the remaining experiments the procedure was the same as above, except that the inversion of 3.396 grams of cane-sugar was not repeated. The results of all experiments are given in Table VI.

Table VI.

Column I.—Weight-normality of the solution.
Column II.—Temperature of rotation.
Column III.—Rotation of I.
Column IV.—Rotation of the solution containing 3.396 grams less sugar per 1000 grams water, corrected for difference in volume.
Column V.—Laevo rotation of 3.5748 grams invert-sugar in Solution I.
Column VI.—Grams of invert-sugar corresponding to loss of 1° rotation.

I.	II.	III.	IV.	V.	VI.
0.10	19°	12°.73	11°.46	0°.39	2.15
0.30	20°	36°.30	35°.03	0°.38	2.17
0.50	20°	58°.90	57°.61	0°.36	2.17
0.70	19°	78°.89	77°.70	0°.35	2.32
0.90	20°	98°.50	97°.31	0°.34	2.34
1.00	20°	107°.40	106°.37	0°.33	2.63

The data above presented afford an accurate and direct method for determining inversion in all cases where loss in rotation can be attributed solely to inversion. There has been observed, in general, in our solutions, a greater and greater loss in rotation as the concentration of the solution increased, and tests by Fehling's method revealed the fact that the inversion in the cell was greater in the case of the more concentrated solutions. The agreement here leaves little room for doubt that the magnitude of the loss in rotation is a true

indication of the extent of the inversion that has taken place. There is no evidence going to show that the rotatory power of cane-sugar is affected by the pressure to which it has been subjected. Such, however, could be considered a possibility.

But there is one cause other than inversion that can with certainty be stated as having an influence on the magnitude of the loss in rotation, namely, dilution of the solution during the experiment, and in the application of the above method, this fact has not been overlooked. To what extent it has been possible to take it into account, and in what way the attempt has been made to distribute the loss in rotation between inversion and dilution will be explained in connection with a discussion of dilution.

THEORETICAL CONSIDERATIONS.

The view generally held regarding the relation between the osmotic pressure of solutions and the elastic pressure of gases seems to be that expressed by Ostwald: "Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified, at the same temperature, without change of volume." Taking this view, the osmotic pressures of concentrated solutions present abnormalities, and the rule above set forth can apply only to dilute solutions.

On the other hand, Morse and Frazer found that when they dissolved a gram-molecular weight of cane-sugar in 1000 grams of water, *i. e.*, in that mass of the solvent which has the unit volume at its temperature of maximum density, the osmotic pressure of that solution at 20° was in close accord with the pressure of a gram-molecular weight of hydrogen confined, at the same temperature, in the space of 1 litre (volume of unit mass of solvent at temperature of greatest density). To repeat, "cane sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state."

Accepting the latter view as the correct one, all the solutions whose osmotic pressures are recorded in this paper were prepared by dissolving a gram-molecular weight of cane-sugar, or a decimal part of the same, in 1000 grams of water, all

weights being corrected for air displacement. Taking the atomic weight of hydrogen as 1.00, the molecular weight of cane-sugar becomes 339.6. The various solutions are designated as *weight-normal*, etc., to distinguish them from solutions made up on the volume basis.

The sugar used was the purest obtainable "rock candy," whose purity was carefully tested by the optical method. To every solution of sugar was added 0.0839 gram of potassium ferrocyanide per 100 grams of water, while to the water outside of the cell was added 0.1239 gram of copper sulphate per 100 grams of water, these quantities being considered as isotonic equivalents. The object of so doing was to provide for the mending of any ruptures occurring in the membrane during the progress of an experiment, and also to diminish the slight tendency of the membrane to dissolve in the solution.

The value given by Morley for the weight of a litre of hydrogen, under standard conditions of temperature and pressure, at latitude 45°, is 0.089873 gram, which corrected to the latitude of Baltimore becomes 0.089826 gram. Dividing 2, the molecular weight of hydrogen, by this value, 0.089826, we obtain 22.265, the pressure of a gram-molecular weight of hydrogen when its volume is reduced to 1 litre at 0°.

If, now, a gram-molecular weight of a substance, dissolved in 1000 grams of water, exerts the same pressure, as osmotic pressure, that a gram-molecular weight of a gas exerts, as elastic pressure, when reduced to a volume of a litre, and if osmotic pressure obeys the law of Gay-Lussac, then the osmotic pressure of a weight-normal solution, at 0°, is 22.265 atmospheres. For temperature t, the value becomes $22.265\ (1 + 0.00367\ t)$, or $22.265 + 0.0817\ t$ atmospheres.

If P represents the osmotic pressure of any solution at the temperature t, then $\frac{P}{22.265 + 0.0817\ t}$ is the weight-normal concentration of the solution. Therefore, $\frac{P}{22.265 + 0.0817\ t} : 1 :: W : M$, or $M = \frac{W(22.265 + 0.0817\ t)}{P}$, where W is the

known weight of the substance which exerts the osmotic pressure P, and M is the molecular weight of the substance.

The molecular weights recorded in the following tables (VII.–XVIII.) have been calculated by means of this formula.

DISCUSSION OF CORRECTIONS.

"*Membrane Formers.*"—As above stated, 0.0839 gram of $K_4Fe(CN)_6.3H_2O$ per 100 grams of water is added to the solution whose osmotic pressure is to be measured, and 0.1239 gram of $CuSO_4.5H_2O$ per 100 grams of water is added to the water outside. These solutions are osmotically equivalent provided the two salts are completely dissociated, and the potassium ferrocyanide dissociates into five ions. However, according to conductivity measurements of Jones and Bassett,[1] potassium ferrocyanide dissociates into eight ions instead of five, and, further, several experiments made by other workers in this laboratory have shown that the osmotic pressure of the ferrocyanide in the cell is in excess of that of the sulphate outside. The magnitude of this overpressure has not yet been determined with certainty, but work is being continued along this line. While it has not been possible to enter a correction in our results for any excess pressure of the potassium ferrocyanide, it is probable that there should be such a correction of from 0.05 to 0.10 atmosphere.

Laws of Boyle and Gay-Lussac.—The question of the deviation from Boyle's law in the case of air under 25 atmospheres has been carefully considered. On account of the unsatisfactory and insufficient experimental data to be obtained in this connection, and further, on account of the fact that such deviation must be small, and is in part, at least, compensated by a deviation in the law of Gay-Lussac, we have not felt justified in attempting to make a correction for this cause.

Adhering of Enclosed Air to Walls of Manometer.—As the mercury rises in the manometer there must be some air caught between the mercury and the walls of the manometer, but we have no means of determining the extent of the error due to this cause.

Expansion of Glass.—The possible expansion of the manom-

[1] Amer. Chem. Jour., 34, 4.

eter tubing under pressure has been taken into consideration. Any such expansion would be expected to manifest itself by a change in the length of the ascending arm of the manometer. Under a pressure of 25 atmospheres the distance from the top of the manometer to the lower scratch was found to be identical with the distance between the same points when there was no pressure being exerted.

Fermentation.—The fermentation of any of the products of inversion in the cell would affect the accuracy of the observations, but no evidence whatever has been obtained indicating any fermentation.

Leakage.—Careful examination of the outside solution after the experiment has shown no leakage of sugar through the membrane.

Dilution.—As stated in the consideration of the relation between loss in rotation and the inversion that has taken place in the cell, any dilution of the cell contents must be taken into account. Only when there is no dilution whatever is the loss in rotation of the solution an exact measure of the quantity of invert-sugar present.

The slight dilution due to the rise of the mercury in the manometer under pressure would not affect appreciably the rotation of the solution, owing to the fact that the total capacity of the largest manometer used is only 0.16 cc., and so much mechanical pressure is constantly brought to bear upon the cell contents and the mercury that the actual distance through which the mercury rises in consequence of the inflow of water is really very small. In the case of the normal solutions where the effect of such dilution would be greatest, the distance through which the mercury rose after sufficient mechanical pressure had been brought to bear to hold the stopper in place was less than one-thirtieth the length of the original air column.

Owing to the fact that the cell walls always contain a little water, some dilution should naturally be expected from this cause. To remove as far as possible all water in the interior of the cell before setting the cell up for a measurement of pressure, the cell is always carefully rinsed out several times with the solution whose pressure is to be determined. But

during the time required for setting up the cell there is necessarily a little dilution due to the attraction of the water in the walls of the cell to the sugar of the solution. The extent of this dilution, and of any further dilution that may be due to a slight compression of the rubber stopper under pressure, or an expansion of the cell, can not be determined.

The most serious source of dilution is that due to the slipping of the rubber stopper or of the manometer upward through the stopper. Attention has already been called to the means taken to prevent both of these sources of error, but, in spite of most careful attention, in a number of experiments considerable dilution has occurred from these causes. It manifests itself by a rise in the position of the top of the manometer as determined repeatedly throughout an experiment, and by a consequent excessive loss in the rotation of the solution. In *every* case recorded, where there has been observed any considerable upward displacement of the manometer during an experiment, there has been observed at the conclusion of the experiment a larger loss in rotation than was observed in experiments with the same solution where there was observed no change in the position of the top of the manometer. If in an experiment no change is observed in the position of the top of the manometer, it is practically certain no dilution has occurred from this cause. But even here the loss in rotation may be affected some by the slight dilution due to the other causes above mentioned. The problem is manifestly a complicated one.

In the experiments recorded in the following tables an attempt has been made to distribute the observed loss in rotation between inversion and dilution. The plan adopted can best be illustrated by a particular example. Take the case of the two experiments with the 0.4 weight-normal solutions, Tables X. and XI. In Expt. 1, the upward displacement of the manometer was 0.3 mm., the loss in rotation 0°.8. In Expt. 2, the upward displacement of the manometer was 1.18 mm., and the loss in rotation was 1°.3. In Expt. 1, the loss in rotation, 0°.8, is taken as a correction for inversion. In Expt. 2, the same correction is applied for inversion, while

0°.5 (1°.3-0°.8) loss in rotation is applied as a correction in the opposite direction for dilution.

The same procedure is followed in the experiments with each of the other concentrations. In the experiment where there has been observed the least rise in the position of the manometer, all loss in rotation is calculated as inversion, while in the other experiment or experiments where there has been observed a greater rise in the position of the manometer, the excess loss in rotation is calculated as dilution.

However, in making the corrections on this basis, the author is not unmindful of the fact that even in the best experiments some of the loss in rotation must be due, not to inversion, but to dilution.

RECORD OF EXPERIMENTS.

In carrying out a measurement of osmotic pressure, before setting away the cell and manometer in their respective places in the bath, preliminary readings are taken on the standard scale of the position of the top of the manometer, the height of the mercury in the manometer, the lower line of reference, Scratch No. 1, the position of the solution in the bulb on the bend of the manometer, and the position of the surface of the water in which the cell is placed. The temperature of the room and the barometric pressure are also observed.

These observations furnish all the data necessary for calculating the pressure of liquids in the cell and manometer, and also the initial pressure on the enclosed air of the manometer.

After placing the cell and manometer in the bath, during the further progress of the experiment, it is necessary only to take readings of the temperature of the water in the bath, the temperature of the air around the manometer, the barometric pressure, and the relative positions of the top of the manometer and the top of the mercury column in the manometer. The barometric readings are corrected for temperature, latitude and altitude. As previously mentioned, all observations of the length of air column in the manometer are corrected for double meniscus, the meniscus of the thread of mercury in the

upper portion of the manometer and that of the mercury column being regarded as spherical.

Values Used in Computations.

Temperature coefficient of gases..... = 0.00367
Coefficient of cubical expansion of mercury..... = 0.0001818
Weight of 1 liter of hydrogen, at 0°, at Baltimore..... = 0.089826 gram
Pressure of a gram-molecular weight of hydrogen, in 1 liter, at 0°..... = 22.265 atmospheres

0.20 Weight-Normal Solution. Experiments 1, 2, 3.

Sugar dissolved in 1000 grams of water.. = 67.92 grams
Volume of solution at 20°..... = 1041.72 cc.
Concentration of solution according to *volume-normal* standard..... = 0.1920

Experiment 1.—
Upward displacement of manometer.... = 2.78 mm.
Loss in rotation..... = 0°.7
Loss in rotation ascribed to inversion... = 0°.5
Loss in rotation ascribed to dilution.... = 0°.2

Experiment 2.—
Upward displacement of manometer.... = 1.44 mm.
Loss in rotation..... = 0°.7
Loss in rotation ascribed to inversion .. = 0°.5
Loss in rotation ascribed to dilution.... = 0°.2

Experiment 3.—
Upward displacement of manometer.... = 0.19 mm.
Loss in rotation, all ascribed to inversion = 0°.5

COMMENTS.

Previous to Expt. 1, after the preparation and development of the membrane already described, cell G had been used for a measurement of the osmotic pressure of a 0.6 weight-normal solution. Up to the time of Expt. 1, the cell had been subjected to the membrane-forming process, in all, 17 hours.

Attention is called to the rapidity with which, in Expt. 3, the pressure reached a maximum.

When molecular weights are determined by osmotic pressure, the accuracy of the results increases with the concentration of the solution. A mistake of 0.10 of an atmosphere in the pressure of a 0.2 weight-normal solution produces an error of 7.08 units in the estimated molecular weight of cane-sugar.

Table VII.

Original wt. normal concentration of solution, 0.2.
Rotation of original solution, 25° ($t = 20°$).
Rotation at conclusion of experiment, 24°.3 ($t = 20°$).
Loss in rotation, 0°.7.
Calibration units of air in manometer, 461.34.
Time of setting up cell, 12.30 P. M., March 3, 1906.

Experiment No. 1.
Manometer used, No. 4.
Capillary depression, 0.02 atmosphere.
Cell used, G.
Resistance of membrane, 271,250 ohms.
Initial pressure, 1.98 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.								
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Loss in rotation. Due to dilution = +0.04. Due to inversion = —0.07.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference b'tween pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
March 3.													
5.50 P. M.	20°.00	21°.64	144.08										
11.00 "	20°.20	22°.00	96.69										
March 4.													
12.00 M.	20°.65	21°.84	95.67	88.57	0.99	0.52		0.02	4.73	4.79	—0.06	343.93	
7.00 P. M.	20°.85	21°.90	95.71	88.59	0.99	0.52		0.02	4.73	4.79	—0.06	344.16	
11.30 "	20°.95	21°.94	95.83	88.69	1.00	0.52		0.02	4.71	4.79	—0.08	345.76	344.96
March 5.													
10.20 A. M.	21°.15	21°.99	95.85	88.69	1.00	0.52		0.02	4.71	4.80	—0.09	345.99	

Table VIII.

Original wt. normal concentration of solution, 0.2.
Rotation of original solution, 25° ($t = 20°$).
Rotation at conclusion of experiment, 24°.3 ($t = 20°$).
Loss in rotation 0°.7.
Calibration units of air in manometer, 402.13.
Time of setting up cell, 4.30 P. M., March 6, 1906.

Experiment No. 2.
Manometer used, No. 6.
Capillary depression, 0.02 atmosphere.
Cell used, G.
Resistance of membrane, 280,000 ohms.
Initial pressure, 2.30 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Loss in rotation. Due to dilution = +0.04. Due to inversion = —0.07.	Corrections. Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
March 6.													
9.10 P. M.	20°.90	22°.04	110.41										
March 7.													
10.30 A. M.	21°.20	22°.19	83.05	76.79	1.00	0.58		0.02	4.81	4.80	+0.01	338.85	
2.30 P. M.	21°.30	22°.25	83.14	76.89	1.00	0.58		0.02	4.80	4.80	0.00	339.67	
4.40 "	21°.30	21°.64	83.18	77.06	1.00	0.58		0.02	4.79	4.80	—0.01	340.38	340.9
9.00 "	21°.35	21°.54	83.62	77.49	1.00	0.58		0.02	4.76	4.80	—0.04	342.58	
March 8.													
10.15 A. M.	21°.73	22°.74	84.09	77.61	0.99	0.58		0.02	4.76	4.80	—0.04	343.02	

Table IX.

Original wt. normal concentration of solution, 0.2.
Rotation of original solution, 24°.9 ($t = 20°$).
Rotation at conclusion of experiment, 24°.4 ($t = 20°$).
Loss in rotation, 0.5.
Calibration units of air in manometer, 402.13.
Time of setting up cell, 4.50 P. M., March 8, 1906.

Experiment No. 3.
Manometer used, No. 6.
Capillary depression, 0.02 atmosphere.
Cell used, G.
Resistance of membrane, 225,400 ohms.
Initial pressure, 2.13 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.					
March 8.													
8.30 P. M.	21°.50	22°.44	86.15										
March 9.													
12.45 A. M.	21°.65	22°.64	83.00	76.63	0.98	0.59	0.07	0.02	4.81	4.81	0.00	339.37	
8.30 "	21°.80	22°.69	83.02	76.64	0.98	0.59	0.07	0.02	4.81	4.81	0.00	339.54	339.74
10.30 "	21°.85	22°.74	83.15	76.74	0.98	0.59	0.07	0.02	4.80	4.81	—0.01	340.31	

0.4 Weight-Normal Solution. Experiments 1, 2.

Sugar dissolved in 1000 grams of water... = 135.84 grams
Volume of solution at 20°..... = 1083.67 cc.
Concentration according to the *volume-normal* standard..... = 0.3691

Experiment 1.—
Upward displacement of manometer.... = 0.30 mm.
Loss in rotation..... = 0°.8
Loss in rotation all ascribed to inversion

Experiment 2.—
Upward displacement of manometer.... = 1.18 mm.
Loss in rotation..... = 1°.3
Loss in rotation ascribed to inversion... = 0°.8
Loss in rotation ascribed to dilution.... = 0°.5

COMMENTS.

In these two experiments, the maximum pressure was reached in 9 and 7 hours respectively.

0.6 Weight-Normal Solution. Experiments 1, 2, 3.

Sugar dissolved in 1000 grams of water.. = 203.76 grams
Volume of solution at 20°..... = 1125.62 cc.
Concentration according to the *volume-normal* standard..... = 0.5322

Experiment 1.—
Upward displacement of manometer.... = 3.78 mm.
Loss in rotation..... = 2°.8
Loss in rotation ascribed to inversion.. = 1°.8
Loss in rotation ascribed to dilution.... = 1°.0

Experiment 2.—
Upward displacement of manometer.... = 0.83
Loss in rotation..... = 1°.9
Loss in rotation, all entered as an inversion correction.....

Experiment 3.—
Upward displacement of manometer.... = 0.64 mm.
Loss in rotation, the whole ascribed to inversion..... = 1°.8

COMMENTS.

In Expt. 2, the maximum pressure was attained in 7 hours after the cell was set up. In the other two, Expts. 1 and 3, a maximum had almost been reached in 7 and 11 hours respectively.

Attention is directed to constant temperature of the solution maintained throughout these experiments.

Table X.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 48°.1 ($t = 16°$).
Rotation at conclusion of expt., 47°.3 ($t = 16°$).
Loss in rotation, 0°.8.
Calibration units of air in manometer, 461.34.
Time of setting up cell, 12.00 M., March 10, 1906.

Experiment No. 1.
Manometer used, No. 4.
Capillary depression, 0.02 atmosphere.
Cell used, G.
Resistance of membrane, 372,300 ohms.
Initial pressure, 6.80 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure, corrected.	Theoretical gas pressure.	Difference b'tween pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.					
March 10.													
6.00 P. M.	21°.45	21°.84	49.41										
8.30 "	21°.48	22°.20	49.19	45.48	1.00	0.58	0.12	0.02	9.62	9.61	+0.01	339.17	
March 11.													
2.00 A. M.	21°.60	22°.39	49.15	45.42	1.00	0.58	0.12	0.02	9.64	9.61	+0.03	338.61	338.73
11.00 "	21°.70	22°.54	49.15	45.40	1.00	0.58	0.12	0.02	9.64	9.61	+0.03	338.72	
12.30 P. M.	21°.75	22°.59	49.14	45.39	1.00	0.58	0.12	0.02	9.65	9.61	+0.04	338.43	

Table XI.

Original wt. normal concentration of solution, 0.4. Experiment No. 2.
Rotation of original solution, 48° ($t = 17°$). Manometer used, No. 6.
Rotation at conclusion of expt., 46°.7 ($t = 17°$). Capillary depression, 0.02 atmosphere.
Loss in rotation, 1°.3. Cell used, G.
Calibration units of air in manometer, 402.13. Resistance of membrane, 277,500 ohms.
Time of setting up cell, 5.15 P. M., March 12, 1906. Initial pressure, 4.30 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Osmotic pressure, corrected.	Theoretical gas pressure.	Difference b'tween pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Due to dilution = +0.10.	Loss in rotation. Due to inversion = −0.12.	Capillary depression.					
March 12.														
8.00 P. M.	22°.00	22°.44	47.31											
March 13.														
12.00 A. M.	22°.10	22°.59	43.27	39.96	1.01	0.64			0.02	9.69	9.63	+0.06	337.44	
10.00 "	22°.15	22°.44	43.29	40.00	1.01	0.64			0.02	9.69	9.63	+0.06	337.50	337.5
12.30 P. M.	22°.20	22°.60	43.29	39.98	1.01	0.64			0.02	9.69	9.63	+0.06	337.55	

Table XII.

Original wt. normal concentration of solution, 0.6. Experiment No. 1.
Rotation of original solution, 69°.2 ($t = 20°$). Manometer used, No. 5.
Rotation at conclusion of expt., 66°.4 ($t = 20°$). Capillary depression, 0.02 atmosphere.
Loss in rotation, 2°.8. Cell used, G.
Calibration units of air in manometer, 442.18. Resistance of membrane, 218,000 ohms.
Time of setting up cell, 5.00 P. M., April 10, 1906. Initial pressure, 11.80 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.									
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Loss in rotation.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
April 10.													
7.45 P. M.	24°.30	24°.40	34.46				Due to dilution = +0.21. Due to inversion = −0.29.						
April 11.													
12.00 A. M.	24°.30	24°.40	31.86	29.24	1.00	0.64		0.02	14.70	14.55	+0.15	336.14	
8.30 "	24°.40	24°.10	31.74	29.16	1.00	0.64		0.02	14.74	14.55	+0.19	335.35	
11.00 "	24°.40	24°.20	31.71	29.12	1.00	0.64		0.02	14.76	14.55	+0.21	334.89	335.32
2.30 P. M.	24°.40	23°.90	31.68	29.13	1.00	0.64		0.02	14.76	14.55	+0.21	334.89	

Table XIII.

Original wt. normal concentration of solution, 0.6. Experiment No. 2.
Rotation of original solution, 69°.2 ($t = 20°$). Manometer used, No. 5.
Rotation at conclusion of expt., 67°.3 ($t = 20°$). Capillary depression, 0.02 atmosphere.
Loss in rotation, 1°.9. Cell used, G.
Calibration units of air in manometer, 442.18. Resistance of membrane, 215,000 ohms.
Time of setting up cell, 5.00 P. M., April 12, 1906. Initial pressure, 10.45 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.								
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference b'tween pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
April 12.													
8.00 P. M.	24°.15	24°.50	31.60										
April 13.													
12.00 A. M.	24°.15	24°.30	31.39	38.82	1.01	0.64	0.30	0.02	14.69	14.54	+0.15	336.20	
9.00 "	24°.20	24°.40	31.39	28.81	1.01	0.64	0.30	0 02	14.70	14.55	+0.15	336.03	
1.00 P. M.	24°.30	24°.55	31.39	28.80	1.01	0.64	0.30	0.02	14.71	14.55	+0.16	335.90	336.07
2.45 "	24°.30	24°.80	31.43	28.81	1.01	0.64	0.30	0.02	14.70	14.55	+0.15	336.13	

Table XIV.

Original wt. normal concentration of solution, 0.6. Experiment No. 3.
Rotation of original solution, 69°.2 ($t = 19°$). Manometer used, No. 6.
Rotation at conclusion of expt., 67°.4 ($t = 19°$). Capillary depression, 0.02 atmosphere.
Loss in rotation, 1°.8. Cell used, G.
Calibration units of air in manometer, 402.13. Resistance of membrane, 272,500 ohms.
Time of setting up cell, 12.30 P. M., April 14, 1906. Initial pressure, 9.00 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.								
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference b'tween pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
April 14.													
4.30 P. M.	24°.10	23°.90	28.79										
7.45 "	24°.10	24°.00	28.63										
11.00 "	24°.10	24°.15	28.54	26.21	0.99	0.66	0.29	0.02	14.74	14.54	+0.20	335.00	
April 15.													
10.00 A. M.	24°.10	24°.00	28.47	26.16	0.99	0.66	0.29	0.02	14.77	14.54	+0.23	334.32	
12.30 P. M.	24°.10	23°.75	28.40	26.12	0.99	0.66	0.29	0.02	14.79	14.54	+0.25	333.87	334.32
3.00 "	24°.10	23°.70	28.41	26.14	0.99	0.66	0.29	0.02	14.78	14.54	+0.24	334.10	
5.30 "	24°.10	23°.70	28.43	26.15	1.00	0.66	0.29	0.02	14.77	14.54	+0.24	334.32	

0.8 Weight-Normal Solution. Experiments 1, 2.

Sugar dissolved in 1000 grams of water... = 271.68 grams
Volume of the solution at 20°..... = 1167.68 cc.
Concentration according to the *volume-normal* standard..... = 0.6834

Experiment 1.—
Upward displacement of manometer.... = 0.32 mm.
Loss in rotation..... = 3°.2
Loss in rotation ascribed to inversion... = 3°.2

Experiment 2.—
Upward displacement of manometer.... = 1.80 mm.
Loss in rotation..... = 3°.9
Loss in rotation ascribed to inversion... = 3°.2
Loss in rotation ascribed to dilution.... = 0°.7

COMMENTS.

The maximum pressure was nearly attained in less than 5 hours, in Expt. 1. In these two experiments there was practically no change of temperature in the water of the bath.

1.0 Weight-Normal Solution. Experiments 1, 2.

Sugar dissolved in 1000 grams of water.. = 339.6 grams
Volume of solution at 20°..... = 1209.81 cc.
Concentration of the solution according to the *volume-normal* standard..... = 0.8266

Experiment 1.—
Upward displacement of manometer..... = 0.88 mm.
Loss in rotation, all ascribed to inversion = 2°.4

Experiment 2.—
Upward displacement of manometer..... = 2.97 mm.
Loss in rotation..... = 4°.0
Loss in rotation ascribed to inversion ... = 2°.4
Loss in rotation ascribed to dilution ..... = 1°.6

COMMENTS.

The cell used in these experiments was B which had been used last year by Morse and Frazer in their measurements of osmotic pressure, and this year for some time in the measurement of the osmotic pressure of grape-sugar solutions. It will be noted that about 59 hours were required for the maximum pressure to develop.

A mistake of 0.1 atmosphere in the osmotic pressure of a weight-normal solution produces an error of only 1.4 units in the estimated molecular weight of cane-sugar.

Table XV.

Original wt. normal concentration of solution, 0.8. Experiment No. 1.
Rotation of original solution, 89° ($t = 19°$). Manometer used, No. 6.
Rotation at conclusion of expt., 85°.8 ($t = 19°$). Capillary depression, 0.02 atmosphere.
Loss in rotation, 3°.2. Cell used, G.
Calibration units of air in manometer, 402.13. Resistance of membrane, 272,500 ohms.
Time of setting up cell, 4.15 P. M., April 2, 1906. Initial pressure, 12.70 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.								Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference b'tween pressure found and calculated.	Molecular weight calculated from osmotic pressure.	
April 2.													
8.30 P. M.	23°.57	24°.30	21.74	19.96	1.01	0.67	0.53	0.02	19.30	19.35	—0.05	340.53	
11.45 "	23°.60	24°.10	21.76	19.99	1.01	0.67	0.53	0.02	19.26	19.35	—0.09	341.27	
April 3.													
8.30 A. M.	23°.60	23°.60	21.70	19.97	1.01	0.67	0.53	0.02	19.29	19.35	—0.06	340 73	340.48
12.30 P. M.	23°.60	23°.80	21.67	19.93	1.01	0.67	0.53	0.02	19.33	19.35	—0.02	340.03	
2.30 "	23°.60	24°.00	21.67	19.92	1.01	0.67	0.53	0.02	19.34	19.35	—0.01	339.85	

Table XVI.

Original wt. normal concentration of solution, 0.8.
Rotation of original solution, 89° ($t = 19°$).
Rotation at conclusion of expt., 85°.1 ($t = 19°$).
Loss in rotation, 3°.9.
Calibration units of air in manometer, 402.13.
Time of setting up cell, 4.30 P. M., April 16, 1906.

Experiment No. 2.
Manometer used, No. 6.
Capillary depression, 0.02 atmosphere.
Cell used, G.
Resistance of membrane, 223,000 ohms.
Initial pressure, 15.10 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Loss in rotation.	Corrections. Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference b'tween pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
April 16.							Due to dilution = +0.15. Due to inversion = —0.53.						
8.00 P. M.	23°.60	23°.50	22.93										
11.50 "	23°.65	23°.85	21.94										
April 17.													
9.00 A. M.	23°.70	23°.50	21.78	20.05	1.01	0.67		0.02	19.35	19.36	—0.01	339.79	
12.30 P. M.	23°.70	23°.30	21.81	20.09	1.01	0.67		0.02	19.31	19.36	—0.05	340.49	
2.30 "	23°.70	23°.30	21.69	19.98	1.01	0.67		0.02	19.43	19.36	+0.07	338.39	339.08
5.00 "	23°.70	23°.20	21.67	19.97	1.01	0.67		0.02	19.44	19.36	+0.08	338.22	
8.00 "	23°.65	23°.10	21.68	19.99	1.01	0.67		0.02	19.42	19.36	+0.06	338.51	

Table XVII.

Original wt. normal concentration of solution, 1.0. Experiment No. 1.
Rotation of original solution, 107°.2 ($t = 22°$). Manometer used, No. 6.
Rotation at conclusion of expt., 104°.8 ($t = 22°$). Capillary depression, 0.02 atmosphere.
Loss in rotation, 2°.4. Cell used, B.
Calibration units of air in manometer, 402.13. Resistance of membrane, 99,100 ohms.
Time of setting up cell, 1.00 P. M., April 27, 1906. Initial pressure, 14.60 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.								
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference b'tween pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
April 28.													
7.30 P. M.	23°.40	24°.70	18.40										
April 29.													
12.00 A. M	23°.50	24°.75	17.69										
9.30 "	23°.60	23°.20	17.41	16.04	1.00	0.67	0.41	0.02	24.34	24.19	+0.15		
1.00 P. M.	23°.55	23°.30	17.38	16.01	1.00	0.67	0.41	0.02	24.40	24.19	+0.21		
7.00 "	23°.55	23°.30	17.37	16.00	1.00	0.67	0.41	0.02	24.41	24.19	+0.22		
April 30.													
12.00 A. M.	23°.55	23°.30	17.33	15.97	1.00	0.67	0.41	0.02	24.47	24.19	+0.28	335.70	335.57
9.00 "	23°.57	23°.93	17.35	15.95	1.00	0.67	0.41	0.02	24.49	24.19	+0.30	335.45	

Table XVIII.

Original wt. normal concentration of solution, 1.0. Experiment No. 2.
Rotation of original solution, 107°.4 (t = 18°). Manometer used, No. 6.
Rotation at conclusion of expt., 103°.4 (t = 18°). Capillary depression, 0.02 atmosphere.
Loss in rotation, 4°. Cell used, B.
Calibration units of air in manometer, 402.13. Resistance of membrane, 84,000 ohms
Time of setting up cell, 3.00 P. M., May 7, 1906. Initial pressure, 17.00 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Loss in rotation.	Corrections. Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
							Due to dilution = +0.37. Due to inversion = —0.41.						
May 8.													
12.00 A. M.	24°.90	24°.50	21.05										
10.30 "	24°.70	23°.40	20.50										
7.30 P. M.	24°.60	23°.90	18.15										
11.30 "	24°.60	24°.50	18.17										
May 9.													
10.15 A. M.	24°.60	24°.14	18.07	16.60	1.00	0.67		0.02	23.88	24.28	—0.40		
2.00 P. M.	24°.60	24°.20	18.00	16.53	1.00	0.67		0.02	23.94	24.28	—0.34		
6.00 "	24°.60	24°.20	18.01	16.54	1.00	0.67		0 02	23.96	24.28	—0.32		
May 10.													
12.00 A. M.	24°.60	24°.10	17.94	16.48	1.00	0.67		0.02	24.05	24.28	—0.23	342.78	342.72
9.00 "	24°.50	23°.90	17.93	16.49	1.00	0.67		0.02	24.05	24.28	—0.22	342.66	

Table XIX.—Summary of Results.

Weight-normal concentration of solution.	Osmotic pressure observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weight. Mean values.
		Experiment 1.			
0.2	4.73	4.79	— 0.06	343.93	
	4.73	4.79	— 0.06	344.16	
	4.71	4.79	— 0.08	345.76	
	4.71	4.80	— 0.09	345.99	344.96
		Experiment 2.			
	4.81	4.80	0.01	338.85	
	4.80	4.80	0.00	339.67	
	4.79	4.80	— 0.01	340.38	
	4.76	4.80	— 0.04	342.58	
	4.76	4.80	— 0.04	343.02	340.90
		Experiment 3.			
	4.81	4.81	0.00	339.37	
	4.81	4.81	0.00	339.54	
	4.80	4.81	— 0.01	340.31	339.74
		Experiment 1.			
0.4	9.62	9.61	0.01	339.17	
	9.64	9.61	0.03	338.61	
	9.64	9.61	0.03	338.72	
	9.65	9.61	0.04	338.43	338.73
		Experiment 2.			
	9.69	9.63	0.06	337.44	
	9.69	9.63	0.06	337.50	
	9.69	9.63	0.06	337.55	337.50
		Experiment 1.			
0.6	14.70	14.55	0.15	336.14	
	14.74	14.55	0.19	335.35	
	14.76	14.55	0.21	334.89	
	14.76	14.55	0.21	334.89	335.32
		Experiment 2.			
	14.69	14.54	0.15	336.20	
	14.70	14.55	0.15	336.03	
	14.71	14.55	0.16	335.90	
	14.70	14.55	0.15	336.13	336.07

Table XIX. (*continued*).

Weight-normal concentration of solution.	Osmotic pressure observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weight. Mean values.
		Experiment 3.			
	14.74	14.54	0.20	335.00	
	14.77	14.54	0.23	334.32	
	14.79	14.54	0.25	333.87	
	14.78	14.54	0.24	334.10	
	14.77	14.54	0.24	334.32	334.32
		Experiment 1.			
0.8	19.30	19.35	—0.05	340.53	
	19.26	19.35	—0.09	341.27	
	19.29	19.35	—0.06	340.73	
	19.33	19.35	—0.02	340.03	
	19.34	19.35	—0.01	339.85	340.48
		Experiment 2.			
	19.35	19.36	—0.01	339.79	
	19.31	19.36	—0.05	340.49	
	19.43	19.36	0.07	338.39	
	19.44	19.36	0.08	338.22	
	19.42	19.36	0.06	338.51	339.08
		Experiment 1.			
1.0	22.47	24.19	0.28	335.70	
	24.49	24.19	0.30	335.45	335.57
		Experiment 2.			
	24.05	24.28	—0.23	342.78	
	24.05	24.28	—0.22	342.66	342.72

Table XX.—Mean Molecular Weight for Each Concentration.

Concentration.	Molecular weight.
0.2	341.87
0.4	338.12
0.6	335.23
0.8	339.78
1.0	339.15
Mean of all determinations	338.83
Theoretical	339.60
Difference	0.77

In the following Table XXI. is given a brief summary of the results obtained by Mr. W. L. Kennon in the measurement of the osmotic pressure of cane-sugar solutions of 0.1, 0.3, 0.5, 0.7 and 0.9 *weight-normal* concentrations.

Table XXI.

Weight-normal concentration of solution.	Osmotic pressure observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressures.	Molecular weight. Mean values.
		Experiment 1.			
0.1	2.50	2.41	0.09	329.09	
	2.50	2.41	0.09	329.14	
	2.52	2.42	0.10	326.58	
	2.52	2.42	0.10	326.58	327.85
		Experiment 2.			
	2.53	2.42	0.11	325.40	
	2.56	2.42	0.14	321.58	
	2.56	2.43	0.13	321.63	
	2.56	2.43	0.13	321.63	322.56
		Experiment 1.			
0.3	7.25	7.21	0.04	337.68	
	7.23	7.21	0.02	338.72	
	7.23	7.21	0.02	338.72	338.37
		Experiment 2.			
	7.21	7.16	0.05	337.36	
	7.21	7.16	0.05	337.53	
	7.17	7.17	0.00	339.70	338.20
		Experiment 1.			
0.5	12.07	12.06	0.01	339.29	
	12.06	12.05	0.01	339.36	
	12.04	12.06	— 0.02	340.16	339.60
		Experiment 2.			
	12.19	12.10	0.09	337.11	
	12.25	12.10	0.15	335.46	
	12.23	12.10	0.13	336.01	336.19

Table XXI. (*continued*).

Weight-normal concentration of solution.	Osmotic pressure observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressures.	Molecular weight. Mean values.
		Experiment 1.			
0.7	16.99	16.92	0.07	338.39	
	16.94	16.92	0.02	339.39	
	16.96	16.95	0.01	339.40	
	16.92	16.96	— 0.04	340.37	339.39
		Experiment 2.			
	16.98	16.89	0.09	338.87	
	16.96	16.89	0.07	339.27	
	16.97	16.95	0.02	339.14	
	16.92	16.98	— 0.06	340.70	339.49
		Experiment 1.			
0.9	21.90	21.87	0.03	339.12	
	21.97	21.87	0.10	338.04	338.58
		Experiment 2.			
	21.98	21.87	0.11	337.89	
	22.05	21.87	0.18	336.82	337.35
				Mean of all determinations.....	335.75

CONCLUSIONS.

The results recorded in the foregoing pages of this paper strengthen the conclusion of Morse and Frazer that the determining factor in osmotic pressure is the numerical relation existing between the molecules of the dissolved substance and of the solvent, rather than the number of molecules of the dissolved substance contained in unit volume of the solution. Cane-sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state. Taking as the standard quantity of the solvent that mass of pure water which has the gas-unit volume, no abnormalties have to be accounted for in the case of the osmotic pressure of solutions of cane-sugar. On this basis the osmotic pressure of these solutions obeys the gas laws.

The margin of experimental error is still too great to admit

of determining whether the correct standard is the volume of the solvent at the temperature of maximum density, or at the temperature at which the pressure is measured.

II. THE SEMIPERMEABLE MEMBRANE OF COPPER COBALTICYANIDE.

INTRODUCTION.

Since the discovery, in 1901, of Morse and Horn[1] that the membrane of copper ferrocyanide could be deposited more successfully and to better advantage electrolytically than by the diffusion method of Pfeffer, no less than twenty-six different precipitates have been examined as to their osmotic activity, with a view to determining which of them might be used to advantage in cases where copper ferrocyanide could not be used for one reason or another.

While quite a number of membranes studied seemed to give promise of being thus useful, as judged simply by pressure measurements with open manometers, or by the rate of overflow of the cell contents under little more than one atmosphere pressure, no conclusions could be drawn definitely as to what would be their conduct were it attempted to use them in the direct measurement of pressure with closed manometers. The latter attempt was not made because of the great difficulty of securing porous cups of unquestionable character, whose walls could be counted upon to give proper support to the membrane. Any conclusions as to the efficiency of a membrane based on results with cells of qsuetionable character must necessarily be of very little value. In this connection it should be noted that many failures to make direct measurements of osmotic pressure have been due, not to the membrane, but to the faulty character of the cell wall in which, or upon which, the membrane was deposited. The importance of keeping this distinction clearly in mind can not be urged too strongly, for many conclusions reached concerning osmotic pressure and its measurement may be entirely erroneous for

[1] Amer. Chem. Jour., 26, 80.

no other reason than that the cell wall did not provide sufficient support for the membrane.

Among the precipitates studied in this laboratory was that of copper cobalticyanide.[1] The results with this membrane were so promising that there was reason to believe that when the problem of the porous cup should have been solved the membrane could be used for the actual measurement of pressure.

When a solution of copper sulphate is completely precipitated by a solution of potassium cobalticyanide, there is formed a beautiful turquoise-blue precipitate of copper cobalticyanide, apparently of composition, $Cu_3CO_2(CN)_{12}$. This precipitate is insoluble in acids, but very soluble in ammonia. With potassium hydroxide it turns green, becoming darker and darker until finally it has the dark appearance of cupric oxide.

Morse and Carver studied the rate of overflow of the cell contents under a pressure of a little more than 1 atmosphere. The membrane of copper cobalticyanide was deposited electrolytically, the anode used being of copper and the cathode of platinum. Tenth-normal solutions of potassium cobalticyanide and of copper sulphate were used as electrolytes, the latter being placed outside the cell. The solution of potassium cobalticyanide in the cell was acidified with acetic acid to neutralize the effect of alkali on the membrane during its deposition. The voltage employed was usually small at the beginning of the membrane deposition, but was gradually increased until it reached about 110 volts. The cells used were bottle shaped and had a capacity of about 200 cc. After the deposition of the membrane, the cell was filled with a normal solution of sugar and placed in a vessel of water, and the rate of overflow observed for a considerable length of time. It amounted, usually, during the first hour to about 6 cc., the rate of overflow decreasing as the solution became more and more diluted by the inflow of water.

Cells of the variety used here were wholly unsuited to the direct measurement of pressure for the reasons above alluded to. Since then much progress has been made in the solution of the problem of the porous cup, and it has been found possible to provide a number of very excellent cells. It was suggested

[1] B. F. Carver: Dissertation, Johns Hopkins University (1903).

by Professor Morse that the membrane of copper cobalticyanide be further studied by an attempt to use it in the actual measurement of osmotic pressure. An account of the beginning that has been made in this direction will be given in the following pages of this paper.

THE CELL USED.

The cell used in this work will be known as Cell L. Before burning it had a length of 9.40 cm., an internal diameter at the open end of 2.49 cm., and an external diameter just below the rim of 3.54 cm. Previous to this work the cell had been used in several experiments with zinc ferrocyanide, after which the cell and its parts were all taken apart, the cement entirely removed, and the membrane dissolved in potassium hydroxide, the last traces being removed by electrolysis. Afterwards the electrolysis was continued until no alkali remained in the walls of the cell. The parts of the cell were then reassembled, it being necessary to provide new parts. The probable effect of the treatment of the cell in this manner on the results of later experiments will be considered further on. It will be unnecessary to describe the apparatus for the removal of air from the cell walls, and that used in the deposition of the membrane. The apparatus and method are identical with those previously described. Cell L was of very fine texture as indicated by the low rate of endosmose when a voltage of 100 was used, with 0.005 normal lithium sulphate solution as electrolyte. It amounted on the average to about 15 cc. per hour. In the deposition of the membrane 0.1 normal potassium cobalticyanide solution was used inside the cell, while a solution of the same concentration of copper sulphate was placed outside. The solution of potassium cobalticyanide was always slightly acidified with acetic acid to neutralize the effect of alkali, care being taken to add the same quantity of acid each time so that the magnitude of the resistance in the circuit during the membrane deposition should not vary on account of the presence of varying quantities of acid. The solution in the cell was renewed every few minutes.

THE EXPERIMENTS.

Preliminary experiments were made with another cell to test

the activity of the membrane. The "overflow" method indicated considerable activity.

In view of the uncertainty as to what current pressure was best suited to the deposition of the membrane it was deemed advisable to make the first experiments with a comparatively low voltage—37 volts.

Accordingly, the membrane deposition was begun as shown in the following record:

Record.

January 20, 1906.

Time.	Current.	Voltage.	Resistance.
3.00 P. M.	0.0050	37.6	7520
3.02 "	0.0080	37.6	4700
3.05 "	0.0044	37.6	8545
3.10 "	0.0034	37.6	11059
3.20 "	0.0026	37.6	14461
3.30 "	0.0022	37.6	17086
3.40 "	0.0020	37.6	18800
3.50 "	0.0019	37.6	19789
4.00 "	0.0019	37.6	19789
4.10 "	0.0018	37.6	20888
4.30 "	0.0018	37.6	20888
4.40 "	0.0016	37.6	23500
4.50 "	0.0016	37.6	23500
5.00 "	0.0016	37.6	23500

The cell was then taken down and placed in distilled water until February 1, when the deposition was continued.

Record.

February 1, 1906.

Time.	Current.	Voltage.	Resistance.
2.40 P. M.	0.0022	37.6	17090
2.45 "	0.0018	37.6	20888
2.50 "	0.0014	37.6	26857
3.00 "	0.0013	37.5	28846
3.10 "	0.0012	37.6	31333
3.20 "	0.0011	37.6	34181
3.30 "	0.0010	37.6	37600
3.40 "	0.0010	37.6	37600
3.50 "	0.0010	37.6	37600
4.00 "	0.0010	37.4	37400
4.10 "	0.0010	37.6	37600
4.20 "	0.0010	37.5	37500
4.30 "	0.0010	37.5	37500
4.40 "	0.0010	37.5	37500

Record.

February 2, 1906.

Time.	Current.	Voltage.	Resistance.
2.50 P. M.	0.0120	37.5	3125
2.55 "	0.0018	37.5	20833
..	....	..	....
3.50 "	0.0010	37.5	37500
4.00 "	0.0010	37.5	37500
4.10 "	0.0010	37.5	37500
4.20 "	0.0010	37.5	37500
4.30 "	0.0010	37.5	37500

The above records are given in detail as showing how uniformly the resistance increased until a maximum was reached, and the behavior which would lead one to expect good results in an attempt to make a measurement with the membrane.

Experiment I.—In accordance with the usual procedure the cell was set up with a preliminary solution of sugar. A 0.5 weight-normal solution made 0.1 normal with potassium cobalticyanide was used. After attaching the manometer to the cell in the usual way, the cell was placed in a 0.1 normal solution of copper sulphate. An initial mechanical pressure of about 1 atmosphere was brought to bear on the cell contents and the mercury in the manometer. The mercury immediately began to fall. Mechanical pressure was again brought to bear, but the mercury again fell, and never showed any tendency to rise. However, such behavior might be expected in a first experiment. The cell was then taken down and placed in distilled water until it was again desired to repeat the membrane-forming process.

Record.—On three following days the deposition was continued for four and one-half hours at the same voltage. At the end of this time the resistance of the membrane had reached 62,100 ohms.

Experiment II.—The cell was again set up with the preliminary solution of sugar. The initial mechanical pressure was about 1 atmosphere. The mercury fell as in the previous experiment and showed no tendency whatever to rise.

On three more consecutive days, in all, five and one-half hours, the membrane was reenforced. At the beginning with a

voltage of 37, the resistance of the membrane was only 8,000 ohms, indicating that the membrane had been considerably ruptured in the last experiment. The record for the third day follows:

Record.

February 9, 1906.

Time.	Current.	Voltage.	Resistance.
2.50 P. M.	0.0010	37.6	37600
3.00 "	0.0006	37.8	63000
3.10 "	0.0004	37.8	94500
3.20 "	0.0004	37.8	94500
3.30 "	0.0004	37.8	94500
3.40 "	0.0003	37.8	126000
3.50 "	0.0003	37.8	126000
4.00 "	0.0003	37.7	125666
4.10 "	0.0003	37.7	125666
4.20 "	0.0003	37.7	125666
4.30 "	0.0003	37.7	125666
4.40 "	0.0003	37.7	125666

The high resistance here reached was taken as an indication of a very satisfactory condition of membrane. This has seemed to be the meaning of high resistance in the case of the copper ferrocyanide membrane.

Experiment III.—The cell was again set up with 0.5 normal cane-sugar, and 0.1 normal membrane-formers. Mechanical pressure was repeatedly brought to bear, which was followed in every case by a fall in the mercury. The mercury never rose. The next day the cell was taken down and set to soak in distilled water.

It was then decided to use a lower voltage for the deposition of the membrane to determine if better results could be obtained.

Record.

February 13, 1906.

Time.	Current.	Voltage.	Resistance.
3.40 P. M.	0.0008	11.6	14500
3.50 "	0.0004	11.6	29000
4.00 "	0.0003	11.6	38666
4.10 "	0.0002	11.6	58000
4.20 "	0.0001	11.6	116000
4.30 "	0.0001	11.6	116000
4.40 "	0.0001	11.6	116000
4.50 "	0.0001	11.6	116000

The deposition was continued after this, on three days, for 5 hours. At the end of this time the resistance was less than in the above record, namely, 38,666 ohms. However, the cell was again set up with the usual solution.

Experiment IV.—The nut was screwed down on the stopper until there was an initial pressure of about 1.5 atmospheres. It then rose about 15 mm. The nut was again screwed down, after which the mercury began to fall and showed no tendency again to rise.

The remaining experiments were made using a voltage of about 112 for the deposition of the membrane, it being thought that possibly a higher voltage than previously used was required, and that better results would possibly be obtained.

Record.

February 20, 1906.

Time.	Current.	Voltage.	Resistance.
3.40 P. M.	0.0082	112.3	13695
3.45 "	0.0033	112.2	34000
3.55 "	0.0022	112.2	51000
4.05 "	0.0019	112.1	59000
4.15 "	0.0017	111.5	65588
4.25 "	0.0016	111.5	69688
4.35 "	0.0015	111.0	74666

Record.

February 21, 1906.

Time.	Current.	Voltage.	Resistance.
3.05 P. M.	0.0047	112	23830
3.10 "	0.0035	112	32000
3.20 "	0.0031	112	36130
3.30 "	0.0030	112	37333
3.40 "	0.0027	112	41481
3.50 "	0.0026	112	43077
4.00 "	0.0022	112	50910
4.10 "	0.0024	112	46666

These records were not what one would consider promising, but the cell was again set up with the usual solutions.

Experiment V.—The behavior of the membrane was as in Expt. 4. There was at one time during the experiment a rise of mercury of about 8 mm., which could easily be accounted for by temperature change.

On February 22, the membrane deposition was resumed for about 1.5 hours. The resistance rose from 41,400 to 111,100 ohms. Voltage, 111.7.

February 23. Time of deposition = 2 hours
Initial resistance..... = 32400 ohms.
Final resistance..... = 80000 ohms.

Experiment VI.—The cell was then set up again after the usual manner. An initial pressure of about 0.5 of an atmosphere was brought to bear. The mercury fell for about 15 minutes, 10 mm. It then began to rise until in 35 minutes it was rising 1 mm. per minute. In 3 hours it rose 107 mm., equivalent to a pressure of 1.5 atmospheres. The theoretical pressure of the solution was about 12 atmospheres. The nut was then screwed down on the stopper until there was a pressure in the manometer of 2.5 atmospheres. The mercury at once began to fall and never afterwards rose again.

CONCLUSIONS.

The above brief study would appear to show that of the three different voltages employed for the deposition of the membrane, that of 37 volts was the most satisfactory. A maximum resistance of more than 125,000 ohms was attained with this voltage. With 12 volts a nearly as good result was obtained, only in this case the current was so small that very little membrane could be deposited without devoting a great deal of time to the deposition. With the voltage of 37 there was a regularity in the increase of the resistance, and the maximum resistance was well maintained. There would seem to have been formed a fairly compact and evenly distributed membrane.

On the other hand it would appear that a current pressure of 110 volts was too high, and that the rapid endosmose of water through the cell wall and membrane was constantly tearing away the membrane, and consequently a constant resistance could not be maintained.

If the resistance developed in the deposition of a membrane is resistance to endosmose, then we should expect a greater resistance in the less porous cell. Experience in this laboratory has shown that in the very porous cells there is low resistance

in the deposition of the membrane, while the resistance becomes greater according as the cell is less porous. Now, if the membrane is successfully deposited, it must cause still greater resistance to endosmose, and if a very high resistance is obtained, it can be taken as a pretty certain indication of the satisfactory condition of the membrane.

If the membrane is strong enough to resist the effects of endosmose, then we should expect the resistance to increase with time, and finally a resistance to be reached which would be maintained constant for a long time. Any further increase in resistance would be very slow on account of the now small additional membrane deposited by the diminished current. If through any cause there should be injury done the membrane, the resistance would decrease. There is probably a voltage at which the endosmose can just be withstood by a given membrane without injury. Past experience in the laboratory has shown that the voltage of 110 is best adapted to the deposition of the copper ferrocyanide membrane, and that good results are not obtained with a much higher voltage. To determine at what voltage the best results can be obtained in the deposition of any other membrane, the problem must be taken up systematically, and some considerable time devoted to it.

That the membrane of copper cobalticyanide is easily injured would seem to be confirmed by the behavior observed in the above experiments. The effect of bringing to bear mechanical pressure on the contents of the cell seems to be injurious. In Expt. 6, a rapid rise of the mercury was observed at the start, but as soon as the nut was screwed down on the stopper, the mercury fell. Subsequent behavior of the membrane upon being again subjected to the membrane-forming process would seem to render this view quite probable. If the membrane be as weak as the above experiments indicate, it can, of course, be of no service in the direct measurement of osmotic pressure.

However, there remains one consideration that makes it extremely doubtful as to how much importance should be attached to the results of the above experiments. After these

experiments had been made, it was decided to remove the cobalticyanide membrane from the cell and replace it by a membrane of copper ferrocyanide, it being desired to use the cell in the exact measurement of the osmotic pressure of cane-sugar solutions. Accordingly, the membrane of copper cobalticyanide was dissolved in ammonia, and the cell afterwards prepared for the deposition of the copper ferrocyanide. But all attempts to secure satisfactory results with the latter membrane in this cell also failed. The cell was set up repeatedly with the preliminary half-normal sugar solution, but never was a pressure of more than 5 atmospheres attained. This failure was probably due to the previous use of the cell with the copper cobalticyanide membrane, and the removal of this membrane as described. This explanation necessarily brings up the question whether the failure to obtain good results with the copper cobalticyanide was not due to the previous use of the cell with the membrane of zinc ferrocyanide. Other attempts made in this laboratory to remove a membrane from a cell and afterwards obtain satisfactory results with the cell have also failed.

These facts serve to emphasize the importance of exercising the greatest care in the selection of the cell in which the study of a membrane is to be made. Probably, if a new cell had been used in the above experiments, much better results would have been obtained with the copper cobalticyanide membrane. On account of there being on hand at the time only a limited number of available cells, and the desirability of making the measurements of pressure recorded in the first part of this paper, the author could not pursue the study further. While the experiments made with the copper cobalticyanide membrane do not settle finally the question of the possibility of using the membrane for the measurement of osmotic pressure, the conclusion seems warranted that this membrane is inferior to the membrane of copper ferrocyanide.

The account above given of a few experiments with the membrane is offered as a further contribution to the knowledge of the subject, which it is hoped will be of service when the study of the membrane of copper cobalticyanide is continued.

BIOGRAPHICAL SKETCH.

Ernest Jenkins Hoffman was born at Jacksonport, Arkansas, April 4, 1879. Since 1884, his home has been at Dallas, North Carolina, where he received his preparatory education, at Gaston College. In the fall of 1897, he entered Davidson College, North Carolina, from which he was graduated, in 1900, with the degree of Bachelor of Arts. In October, 1901, he entered the Johns Hopkins University as a student in physics and mathematics. Since 1902, he has been a graduate student in chemistry, with physical chemistry and physics as his subordinate subjects. Throughout his connection with the university he has held a North Carolina Hopkins Scholarship.